Spectral Lineshapes

<div align="right">**8**</div>

The lineshape function $\phi(\nu)$ characterizes the relative variation in the spectral absorption coefficient with frequency and appears directly in Beer's Law:

$$\left(\frac{I}{I^0}\right)_\nu = \exp(-S\phi_\nu P_i L) \tag{8.1}$$

This variation with frequency is caused by broadening mechanisms in the medium. An understanding of these mechanisms allows accurate predictions of the lineshape function. Likewise, a measurement of the lineshape function, and the center frequency, ν_0, can be used to determine properties of the medium such as temperature, pressure, and velocity.

8.1   Lineshape Introduction

The lineshape function has been defined so that its integral over frequency is unity,

$$\phi(\nu) = \frac{k_\nu}{\int\limits_{\text{line}} k_\nu d\nu}, \tag{8.2}$$

so that

$$\int_{-\infty}^{+\infty} \phi(\nu)\,d\nu = 1. \tag{8.3}$$

A typical lineshape of an isolated absorption line centered at ν_0 is shown in Fig. 8.1 as a function of frequency.

The lineshape has a maximum value $\phi(\nu_0)$ at the center frequency ν_0. The width of the feature, $\Delta\nu$, is defined by the width at half the maximum value (the fullwidth
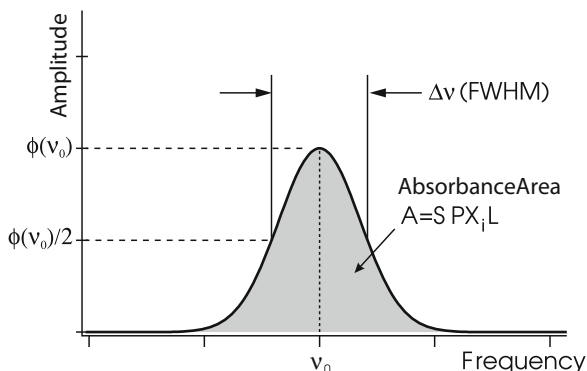
Fig. 8.1 Sample lineshape as a function of frequency

at half maximum, or, FWHM). Note that the halfwidth at half maximum, HWHM, is also used in many texts. The integral in Eq. (8.3) is defined to have no dimensions. Since the units of dv are typically either cm^{-1} or s^{-1}, $\phi(v)$ will have units of cm or s, respectively.

It is often convenient to investigate the lineshape and other absorption parameters by converting transmission or absorption into *absorbance*, where absorbance is defined as

$$\alpha(v) = -\ln\left(\frac{I}{I^0}\right)_v = S\phi_v P_i L = S\phi_v PX_i L, \tag{8.4}$$

where X_i = mole fraction of the absorbing species i. Note that absorbance has no units.

8.2   Line Broadening Mechanisms

Broadening of an absorption feature occurs due to physical processes within the medium that perturb the transition's energy levels or the way in which individual atoms and molecules interact with light. If this effect is the same for all atoms of the species, the broadening is said to be *homogeneous*. If, however, there are separate classes or subgroups for which the interaction varies, the broadening is said to be *inhomogeneous* or heterogeneous. This subtle difference will become more clear when examining the types of broadening mechanisms.

The energy of an optical transition is equal to the energy difference between two states. The Heisenberg Uncertainty Principle relates the uncertainty of these energy levels to their lifetimes [1]. The uncertainty in the energy of level i is limited by

$$\Delta E_i \geq \frac{h}{2\pi\tau_i} \tag{8.5}$$

where τ_i is the lifetime of level i. The lifetimes of the upper and lower states, τ' and τ'', respectively, can be combined to give the total energy uncertainty ΔE of a transition. Thus, there is a range of energies over which the transition has a non-zero probability of being measured. Since $\Delta E = h\Delta\nu$, that range is characterized by a linewidth (FWHM) given (in units of frequency) by:

$$\Delta\nu = \frac{1}{2\pi}\left(\frac{1}{\tau'} + \frac{1}{\tau''}\right) \tag{8.6}$$

Since the Uncertainty Principle applies to all atoms in the same way, lifetime broadening is *homogeneous*. The lineshape function can be derived by modelling the atomic system as a damped oscillator. It takes the form of a Lorentzian function:

$$\phi_L(\nu) = \frac{1}{2\pi}\frac{\Delta\nu}{(\nu - \nu_0)^2 + \left(\frac{\Delta\nu}{2}\right)^2} \tag{8.7}$$

The Lorentzian lineshape function at linecenter is

$$\phi_L(\nu_0) = \frac{2}{\pi\Delta\nu}. \tag{8.8}$$

Another form of Eq. (8.7) is

$$\phi_L(\nu) = \phi_L(\nu_0)\frac{1}{1 + 4(\frac{\nu-\nu_0}{\Delta\nu})^2}. \tag{8.9}$$

There are different mechanisms that lead to broadening of spectroscopic transitions. Some of these mechanisms are described below.

8.2.1 Natural Broadening

In the absence of interactions with other atoms (e.g., via collisions), the lifetime of an atom in a particular level is determined by spontaneous emission [2]:

$$\Delta\nu_N = \frac{1}{2\pi}\left(\frac{1}{\tau_i} + \frac{1}{\tau_j}\right) \tag{8.10}$$

$$= \frac{1}{2\pi}\left(\sum_k A_{ik} + \sum_k A_{jk}\right) \tag{8.11}$$

This is the sum of the Einstein A coefficients for all downward transitions from the two levels of the transitions i and j. Thus, the sum is over all k such that $E_k < E_i$ or E_j. Note that if the lower level, level j, is the ground state, there can be no radiative

decay and its contribution to the halfwidth is zero. The subscript N indicates that the FWHM is due to natural broadening which is described by the Lorentzian lineshape function in Eq. (8.7).

8.2.2 Collisional Broadening (Pressure Broadening)

Molecules (or atoms) interact with each other via collisions. During a collision, energy may be transferred among various energy modes within and between molecules, thus changing the molecular state each molecule exists in. As a result, collisions can reduce the average lifetime of a molecule in a state below that of the natural lifetime. According to Eq. (8.6), shortening the lifetime τ_i of a molecule in level i leads to greater uncertainty, and thus a broader absorption lineshape. Hence, the more frequently collisions occur, the more lifetimes are shortened and transitions are broadened. This relationship between collision frequency and transition breadth is the fundamental mechanism underlying collisional (or pressure) broadening.

A collision can be modelled as occurring when two molecules approach each other within a certain distance called the optical collision diameter. If the diameters of molecules A and B are defined as σ_A and σ_B, respectively, the optical collision diameter is given by

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \tag{8.12}$$

The associated optical cross-section area is $\pi(\sigma_{AB})^2$. Note that this cross-section may be significantly different than the cross-sections for collisions between A and B that give rise to other phenomena (e.g., the elastic collision cross-section). The number of collisions per second *of a single B* with all A is given by

$$Z_{AB} = n_A \pi \, \sigma_{AB}^2 \, \bar{c} \tag{8.13}$$

where n_A is the number density of species A and $\bar{c}$ is the mean relative speed of the molecules given by

$$\bar{c} = \left(\frac{8kT}{\pi \, \mu_{AB}} \right)^{1/2} \tag{8.14}$$

The reduced mass, μ_{AB}, is a function of the masses of A and B

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} \tag{8.15}$$

The total collision frequency (*of a single B*) for a variety of different collision partners is obtained by summing over the different species:

$$Z_B = \sum_A n_A \pi \, \sigma_{AB}^2 \left(\frac{8kT}{\pi \, \mu_{AB}} \right)^{1/2} \tag{8.16}$$

Note that for a pure gas, i.e. all B, Eq. (8.16) simplifies to the expression $Z_B = n_B \pi \sigma_{BB}^2 (8kT/\pi \mu_{BB})^{1/2}$. By introducing the ideal gas law, $P = nkT$, we can rewrite Eq. (8.16) for the single-molecule collision frequency as

$$Z_B = P \sum_A X_A \pi \, \sigma_{AB}^2 \left(\frac{8}{\pi \, \mu_{AB} kT} \right)^{1/2} \tag{8.17}$$

where P is the total pressure and X_A is the mole fraction of species A. Using Eq. (8.6) with $1/\tau' = 1/\tau'' = Z_B$, it follows that $\Delta\nu_C$, the FWHM due to collisional broadening, is given by

$$\Delta\nu_C = \frac{Z_B}{\pi}. \tag{8.18}$$

The frequency uncertainty due to collisional effects, $\Delta\nu_C$, is the lineshape's halfwidth (FWHM). This net uncertainty for the interrogated species, B, is often modelled as the product of the system pressure and sum of the mole fraction for each perturbing species A multiplied with its process-dependent collisional broadening coefficient $2\gamma_{B-A}$

$$\Delta\nu_C = P \sum_A X_A 2\gamma_{B-A}. \tag{8.19}$$

Thus, the collisional width of an absorption transition is directly proportional to pressure. The standard notation for the different broadening coefficients is $2\gamma_{B-A}$, where B is the molecule whose lineshape is being studied and A is the collision partner (or perturber) that interacts with species B to broaden its absorption line. Thus, $2\gamma_{CO-CO}$ is the broadening coefficient for CO–CO collisions (self-broadening, $2\gamma_{self}$), and $2\gamma_{CO-N_2}$ is the coefficient for CO lineshape broadening due to collisions with N_2 (nitrogen-broadening). Mass-averaged O_2 and N_2 coefficients are contained in air-broadening coefficients, $2\gamma_{CO-Air}$. Values of 2γ are published for specific transitions and specific collision partners.

If P has units of atmospheres, and $\Delta\nu_C$ has units of s^{-1} then $2\gamma_B$ is defined by

$$2\gamma_B = 1.013 \times 10^6 \, \sigma_{AB}^2 \left(\frac{8}{\pi \, \mu_{AB} kT} \right)^{1/2} \tag{8.20}$$

where all parameters are in *cgs* units. The optical cross-section $\pi\sigma_{AB}^2$ and reduced mass μ_{AB} depend on the molecule of interest and its various collision partners, though typical values for small molecules are $2\gamma \approx 0.1 \, cm^{-1}/atm$, at room temperature.

Example: Pressure Broadening of CO

Calculate the collisional halfwidth (FWHM) for the $R(9)$ line of CO's second overtone for 50 ppm of CO in air at 300 K and 1.0 atm pressure. The standard species populations in air are 77 % N_2, 21 % O_2, 2 % H_2O (for 85 % standard humidity), and 380 ppm CO_2. The broadening coefficients and species mole fractions are listed in the following table. According to Eq. (8.19), the colli-

Species, A	Mole fraction, X_A	$2\gamma_{CO-A}(300 \text{ K}) \text{ cm}^{-1}/\text{atm}$
N_2	0.77	0.116
H_2O	0.02	0.232
CO	50e−6	0.128
CO_2	380e−6	0.146
O_2	0.21	0.102

sional halfwidth for this CO transition is:

$$\Delta\nu_C = P(X_{N_2} \cdot 2\gamma_{CO-N_2} + X_{H_2O} \cdot 2\gamma_{CO-H_2O} + X_{CO} \cdot 2\gamma_{CO-CO}$$
$$+ X_{CO_2} \cdot 2\gamma_{CO-CO_2} + X_{O_2} \cdot 2\gamma_{CO-O_2})$$
$$= 0.114 \text{ cm}^{-1}$$

The variation of the broadening coefficient 2γ with temperature is often modeled using the following approximation

$$2\gamma(T) = 2\gamma(T_0) \left(\frac{T_0}{T}\right)^N \tag{8.21}$$

where T_0 is the reference temperature, typically 296 or 300 K, $2\gamma(T_0)$ is the broadening coefficient at the reference temperature, and N is the temperature coefficient, which is generally less than 1 and typically 0.5–0.8. Inspection of Eq. (8.20) reveals that $N = 0.5$ when σ_{AB} is constant, independent of T, but in fact σ_{AB} is typically a weak function of T.

In the absence of actual data, useful approximations are that $2\gamma(300) \approx 0.1 \text{ cm}^{-1}/\text{atm}$ for molecules (atoms tend to have larger values) and $N = 0.5$. An exception, however, is NO, whose broadening coefficients for electronic transitions are $2\gamma(300) \approx 0.5 \text{ cm}^{-1}/\text{atm}$. Another exception is H_2O for which 2γ and N vary widely, N can even be < 0 for high-J transitions (see Chap. 14).

Table 8.1 Some collisional broadening coefficients 2γ [cm^{-1}/atm] in Argon and Nitrogen at 300 K

Species	Wavelength [nm]	Ar	N$_2$
Na	589	0.70	0.49
K	770	1.01	0.82
Rb	421	2.21	1.51
OH	306	0.09	0.10
NH	335	0.038	
NO	225	0.50	0.58
NO	5300	0.09	0.12
CO	4700	0.09	0.11
HCN	3000	0.12	0.24

Table 8.2 Some collisional broadening coefficients 2γ [cm^{-1}/atm] in Argon and Nitrogen at 2000 K

Species	Wavelength [nm]	Ar	N$_2$
NO	225	0.14	0.14
OH	306	0.034	0.04
NH	335	0.038	

Tables 8.1 and 8.2 contain broadening coefficients for a variety of species at 300 and 2000 K, respectively. Note that there are some radicals listed here that are not stable at 300 K. However, it is common to extrapolate values of 2γ down to 300 K to facilitate comparisons. Some molecules, like OH, have a strong J (rotational quantum number) dependency on 2γ, while others such as NO do not.

Collisional broadening follows the Lorentzian spectral distribution in Eq. (8.7). The total halfwidth for the Lorentzian lineshape can be determined by adding the natural and collisional halfwidths, $\Delta v = \Delta v_N + \Delta v_C$. However, Δv_C is usually much greater than the natural broadening, so Δv_N can often be neglected.

8.2.3 Doppler Broadening

When a molecule has a velocity component in the same direction as the propagation of a beam of light, there will be a shift in the frequency at which it will absorb a photon. This effect is called the Doppler shift. The molecules of any gas are in constant motion and the distribution of their random velocities (achieved in the absence of collisions, see 8.5.1) is described by the Maxwellian velocity distribution function. We can consider each group of molecules with the same velocity component to be part of a velocity class. The Maxwellian velocity distribution function tells us what portion of the molecules are in each class. Each velocity class will have its own

Doppler shift. Thus the distribution function leads directly to an *inhomogeneous* (meaning it varies with frequency) lineshape function with a Gaussian form:

$$\phi_D(v) = \frac{2}{\Delta v_D} \left(\frac{\ln 2}{\pi} \right)^{1/2} \exp \left\{ -4 \ln 2 \left(\frac{v - v_0}{\Delta v_D} \right)^2 \right\} \tag{8.22}$$

The Gaussian lineshape function at linecenter is

$$\phi_D(v_0) = \frac{2}{\Delta v_D} \left(\frac{\ln 2}{\pi} \right)^{1/2} \tag{8.23}$$

The Doppler halfwidth (FWHM) Δv_D is given by

$$\Delta v_D = v_0 \left(\frac{8kT \ln 2}{mc^2} \right)^{1/2}, \tag{8.24}$$

for which a more convenient form is

$$\Delta v_D = v_0 (7.1623 \times 10^{-7}) \left(\frac{T}{M} \right)^{1/2}, \tag{8.25}$$

where T is in Kelvins and M is the molecular weight in grams/mole. The Doppler halfwidth Δv_D is to be used with Eq. (8.22) and never with (8.7).

The Gaussian lineshape can also be described in normalized terms as an exponential relationship,

$$K_D(x) = \exp(-x^2), \tag{8.26}$$

where

$$x = \frac{(v - v_0)}{\Delta v_{D,1/e}} \tag{8.27}$$

is the normalized frequency detuning relative to the linecenter frequency, v_0, and $\Delta v_{D,1/e}$ is the $1/e$ halfwidth,

$$\Delta v_{D,1/e} = v_0 \sqrt{\frac{2kT}{mc^2}}. \tag{8.28}$$

Figure 8.2 compares Gaussian (Doppler; inhomogeneous) and Lorentzian (collisional and natural; homogeneous) lineshapes which have the same FWHM and by definition [Eq. (8.3)] the same area. The Gaussian lineshape has a peak value which is about 50 % higher than the Lorentzian, but it drops off much faster in the wings. The molecules of each velocity class will also have some finite lifetime and thus some Lorentzian halfwidth. If the Lorentzian halfwidth is much smaller than the Gaussian halfwidth, the Lorentzian component can be ignored, and vice versa.
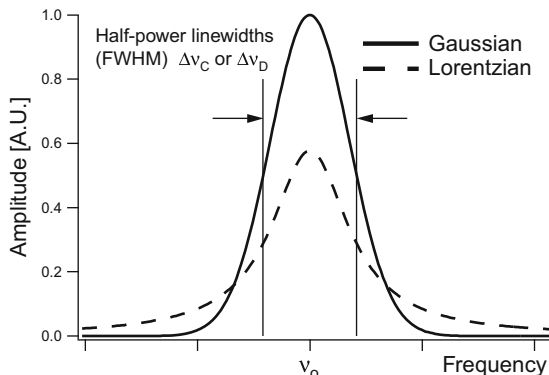
Fig. 8.2 Comparison of Gaussian and Lorentzian lineshapes with the same FWHM

8.2.4 Stark Broadening

Plasmas are characterized by the presence of charged particles (ions and electrons) which exhibit long range Coulomb forces. These forces can perturb the energy levels causing significant broadening, particularly in atomic hydrogen and other light atoms. Both numerical and experimental results are published for specific transitions as a function of electron number density. See the book by Griem [3] for a detailed description.

8.2.5 Artifactual/Instrument Broadening

A measured lineshape can be broader than expected based on the conditions found in a medium. Broadening can be caused by the way in which a measurement is made and thus is an artifact of the experiment. One common example is where an instrument such as a monochromator has insufficient resolution to measure an actual lineshape. This low resolution causes the measured profile to look broader than it really is. Another example is power broadening where a laser is strong enough to perturb the populations of the molecular states (this effect is often referred to as saturation) and thereby modify the frequency distribution of the absorption coefficient. A third example is transit-time broadening where the interaction between the molecules and the light is limited to a time comparable to (or less than) the lifetime determined by collisions or natural emission. As an example, the transit time for a gas moving at velocity V across a laser beam of diameter D is D/V; this leads to an apparent broadening for absorption lines of $\Delta \nu_{\text{transit}}(\text{FWHM}) \approx V/D$ in the case of a top hat intensity distribution [2].

8.3   Voigt Profile

8.3.1   Analytical Expressions

In the common case in which both Doppler and collisional broadening are significant and neither can be neglected, the appropriate lineshape will be a combination of the two. If we assume that the effects of Doppler and collisional broadening are decoupled, we can view each velocity class to be collisionally broadened. This leads to a lineshape that is a convolution of Doppler and collisional broadening [4] (assuming natural broadening is much less than collisional broadening, $\Delta \nu_N \ll \Delta \nu_C$).

$$\phi_V(\nu) = \int_{-\infty}^{+\infty} \phi_D(u)\, \phi_C(\nu - u)\, du \tag{8.29}$$

This convolution is called the Voigt function. Before inserting relations for ϕ_D and ϕ_C, we define some useful parameters:

(1) Voigt "a" parameter

$$a = \frac{\sqrt{\ln 2}\; \Delta \nu_C}{\Delta \nu_D} \tag{8.30}$$

(2) nondimensional line position, w

$$w = \frac{2\sqrt{\ln 2}\; (\nu - \nu_0)}{\Delta \nu_D} \tag{8.31}$$

(3) linecenter magnitude, $\phi_D(\nu_0)$, the magnitude of Eq. (8.22) at ν_0

$$\phi_D(\nu_0) = \frac{2}{\Delta \nu_D} \sqrt{\frac{\ln 2}{\pi}} \tag{8.32}$$

(4) integral variable, y

$$y = \frac{2\, u\, \sqrt{\ln 2}}{\Delta \nu_D} \tag{8.33}$$

With these parameters, Eq. (8.29) becomes

$$\phi_V(\nu) = \phi_D(\nu_0)\, \frac{a}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-y^2)\, dy}{a^2 + (w - y)^2} \tag{8.34}$$

$$= \phi_D(\nu_0)\, V(a, w) \tag{8.35}$$

where $V(a, w)$ is the famous "Voigt function." The a parameter indicates the relative significance of Doppler and collisional broadening, with a increasing as

the effects of collisional broadening increase. The w parameter is a measure of the distance from linecenter. The integral can be calculated using standard mathematical routines, but it is common to make use of existing tables for this function.

Note that at the linecenter, where $w = 0$, $V(a, w)$ reduces to

$$V(a, 0) = \exp(a^2)\text{erfc}(a) \qquad (8.36)$$

$$= \exp(a^2)[1 - \text{erf}(a)] \qquad (8.37)$$

where erf(a) is the error function.

8.3.2   Numerical Approximations

There are many different numerical approximations for the Voigt lineshape that have been published. One of the most accurate and quickest to calculate is the algorithm published by Humlíček (*J. Quant. Spectrosc. Radiat. Transfer*, Vol. 27, No. 4, pp. 437–444, 1982). The algorithm can be processed using standard programs such as Igor Pro, Matlab, and the C language. Appendix C contains an example Matlab *.m file for calculating the normalized Voigt profile.

8.4   Line Shifting Mechanisms

Just as there are physical mechanisms that broaden absorption lines, there are processes by which the lineshapes are shifted in frequency. Two of these shift mechanisms, similar to broadening, are pressure shift and Doppler shift.

8.4.1   Pressure Shift of Absorption Lines

Interactions between two collision partners can have a perturbing effect on the intermolecular potential of the molecule whose lineshape is being studied. Changes in the intermolecular potential lead to differences in the energy level spacings, and hence the linecenter frequencies of the different transitions. These differences from the equilibrium linecenter values that result from collisions are known as pressure shift. Just as in Eq. (8.19), where the collisional halfwidth, $\Delta\nu_C$, is proportional to the pressure and a broadening coefficient, 2γ, the expression for pressure shift depends directly on pressure but contains the shift coefficient δ instead. Both 2γ and δ have units of cm^{-1} per atm.

$$\Delta\nu_S = P \sum_A X_A \delta_A \qquad (8.38)$$

The shift coefficient also scales from a reference temperature similarly to the broadening coefficient, but with a different temperature exponent, M.

$$\delta_A(T) = \delta_A(T_0) \left(\frac{T_0}{T}\right)^M \tag{8.39}$$

Note that while $2\gamma > 0$, the pressure shift can be either negative or positive. Average values for near-infrared H_2O spectra are $\delta \approx -0.017\,\text{cm}^{-1}/\text{atm}$ and $M \approx 0.96$.

8.4.2   Doppler Shift Measurements of Velocity

For gases that have a bulk velocity relative to an incident laser beam, the entire Voigt profile is shifted by

$$\frac{\delta\nu}{\nu_0} = \frac{u}{c} \tag{8.40}$$

where u is the bulk or mean speed in the laser direction and c is the speed of light. Measurements of this frequency shift provide a non-intrusive means of measuring gas velocities. This capacity is especially attractive for high speeds and low densities where conventional laser Doppler anemometry (with particles) is not feasible.

8.5   Lineshapes Beyond the Voigt Profile

The Voigt profile assumes that Doppler and collisional broadening are independent/uncorrelated and does not account for velocity-changing collisions. In some cases, these assumptions can lead to relatively large errors (typically 1–10 % of peak values) in modeling the lineshape of measured spectra. This section will briefly discuss the underlying physics responsible for these errors and introduce a few advanced lineshape profiles that address these processes. See Sect. 14.3 for a working example.

8.5.1   Line Narrowing Mechanisms

While collisional broadening is usually more significant, collisions can also narrow lineshapes via two primary mechanisms: (1) Dicke narrowing [5] and (2) speed-dependent (i.e., heterogeneous) collisional broadening. These processes, more generally referred to as "collisional narrowing," lead to larger peak absorbances and smaller FWHM. Collisional narrowing is most significant for molecules with large rotational-energy spacing (e.g., H_2O, HF, HCN) and at temperatures where the thermal energy kT is small compared to the spacing between rotational energy levels ($\sim 2BJ''$). In this case only strong collisions are rotationally inelastic, and therefore, state-changing collisions are less common (i.e., γ is small).

Dicke narrowing describes a collision-induced reduction of the Doppler width [compared to that calculated using Eq. (8.25)] that results from velocity-changing collisions reducing the average thermal velocity of the absorber with respect to the photon. Recall, the Maxwellian velocity distribution does not account for collisions. Dicke narrowing is expected to be observed at modest number densities where the mean free-path is comparable to $\lambda/2\pi$ where λ is the wavelength of the transition [6]. Dicke narrowing is insignificant when collisional broadening dominates the lineshape (e.g., at high pressures).

Speed-dependent collisional broadening refers to collisional broadening that depends on the speed of the absorber/emitter (i.e., which velocity class it belongs to) and, therefore, is heterogeneous/inhomogeneous. For example, a molecule moving at 1 m/s is likely to experience a very different type of collision (e.g., head-on vs. glancing) than a molecule traveling at 1000 m/s. Despite its name, speed-dependent broadening leads to a narrower lineshape compared to lineshape models that assume homogeneous collision broadening (e.g., Lorentzian, Voigt).

8.5.2   Rautian and Galatry Profiles

The Rautian [7] and Galatry [8] profiles address Doppler and collisional broadening in the same manner as the Voigt profile; however, they also address Dicke narrowing through either hard- or soft-collision models, respectively. The hard-collision model assumes that the velocity of the radiator after a collision is uncorrelated with its velocity prior to the collision while the soft-collision model assumes many collisions are needed to significantly alter the velocity of the radiator. Both lineshape models address Dicke narrowing through one additional (compared to the Voigt) parameter β, commonly expressed in units of cm^{-1} or cm^{-1}/atm, that represents the frequency of velocity-changing collisions. β is lineshape-model specific, and thus, cannot be used interchangeably between the Rautian and Galatry profiles. If $\beta = 0$, both the Rautian and Galatry profiles reduce to the Voigt profile.

8.5.3   Speed-Dependent Voigt Profile

In reality, Doppler and collisional broadening are not independent processes and, in fact, collisional broadening depends on which velocity class an absorber/emitter belongs to. The speed-dependent Voigt profile [9] acknowledges this by introducing a speed-dependent broadening coefficient γ_2, and γ represents the speed-averaged collisional-broadening coefficient. The speed-dependent Voigt also models the speed dependence of the pressure-shift by introducing a speed-dependent pressure shift coefficient δ_2. If speed-dependent effects are negligible (i.e., $\gamma_2 = \delta_2 = 0$), the speed-dependent Voigt profile reduces to the standard Voigt profile.

8.6   Quantitative Lineshape Measurements

The size and shapes of different transitions can be used to make quantitative measurements of species concentration, pressure, temperature, and flow velocity.

8.6.1   Species Concentration and Pressure

A measurement of the integrated absorbance,

$$A_i = \int_{-\infty}^{+\infty} \alpha(v)dv \tag{8.41}$$

or area under the absorption transition, can be used to calculate the species molefraction, X_j, and the pressure, P. The integral in Eq. (8.41) removes the normalized contribution of the lineshape, reducing Eq. (8.4) to

$$A_i = S_i P X_j L \tag{8.42}$$

where S_i is the line strength of the transition, X_j is the molefraction of the absorbing species, P is the pressure, and L is the pathlength. When $S_i PL$ is known, the species concentration is then given by

$$X_j = \frac{A_i}{S_i PL} \tag{8.43}$$

Similarly, if $S_i X_j L$ is known, the pressure is determined by

$$P = \frac{A_i}{S_i X_j L} \tag{8.44}$$

8.6.2   Temperature

There are two lineshape techniques available for measuring the temperature. The first can be used in Doppler-limited applications, where the pressure broadening is negligible. For these applications, the width of the absorption lineshape, or FWHM, can be related directly to the temperature of the absorbing species via Eq. (8.24).

For measurement regimes in which pressure broadening cannot be ignored, a two-line technique can be used. Earlier, it was demonstrated that a line strength for a particular transition has a temperature dependency [Eq. (7.74)]. Taking the ratio of the integrated absorbance area for two transitions removes the pressure and species concentration parameters, leaving only the temperature and lower-state energies for the respective transitions. Since the lower-state energies are typically known (either by quantum mechanical calculation or, more commonly, from tabulations), the temperature can be inferred. The ratio of the integrated areas, R, is related to the temperature by

$$R = \frac{S(T, \nu_1)}{S(T, \nu_2)} = \frac{S(T_0, \nu_1)}{S(T_0, \nu_2)} \exp\left[-\left(\frac{hc}{k}\right)(E_1'' - E_2'')\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{8.45}$$

where ν_1, ν_2, E_1'', and E_2'' are the linecenter frequencies and lower-state energies for the two transitions, $S(T_0, \nu_1)$ and $S(T_0, \nu_2)$ are the strengths of the two lines at the reference temperature T_0, and the induced emission terms have been neglected. Thus, the temperature is

$$T = \frac{\frac{hc}{k}(E_2'' - E_1'')}{\ln R + \ln \frac{S_2(T_0)}{S_1(T_0)} + \frac{hc}{k}\frac{(E_2'' - E_1'')}{T_0}} \tag{8.46}$$

Differentiating Eq. (8.45) yields the temperature sensitivity for a given line pair at a specific temperature in percent per Kelvin:

$$\frac{1}{R}\frac{dR}{dT} \ [\%/\text{K}] = \left(\frac{hc}{k}\right)\frac{(E_1'' - E_2'')}{T^2} \times 100 \tag{8.47}$$

This shows that a large $\Delta E''$ is desirable, to enhance sensitivity, regardless of the temperature. There are additional factors, however, which must be considered. The absorbance of each transition (α_1 and α_2) must be properly bounded. A good rule of thumb is $0.1 < \alpha < 2.3$. This means that for a given partial pressure, path length, and lineshape, the two linestrengths, $S_1(T)$ and $S_2(T)$, will be bounded. Generally, a large difference between E_1'' and E_2'' results in a large difference between $S_1(T)$ and $S_2(T)$. Thus, we see that a tradeoff exists between acceptable absorbance levels and temperature sensitivity.

8.6.3   Examples

Nitric Oxide, NO
Nitric oxide, NO, is a common species found in combustion flows. It has an electronic transition ($A^2\Sigma - X^2\Pi$) near 225 nm (44,000 cm^{-1}) in the UV region. Some typical values (in cm^{-1}) for the halfwidths are shown below for a pressure of 1 atm and two different temperatures.

T [K]	$\Delta\nu_N$	$\Delta\nu_C$	$\Delta\nu_D$
300	$\sim 5\times10^{-5}$	0.58	0.10
2000		0.14	0.26

Since neither Doppler nor collisional broadening is dominant, Voigt functions are necessary at both temperatures to accurately describe the lineshape function. It is clear that Doppler broadening becomes more significant with increasing temperature (scales with $T^{1/2}$). Likewise, collisional broadening becomes more

significant with increasing pressure (scales approximately with $P/T^{1/2}$). Note that the collisional broadening coefficient for NO's electronic transition is relatively high compared to other molecules.

Because Doppler broadening is proportional to the transition frequency, it becomes less significant for IR spectroscopy. NO has a vibrational band at 5.3 μm. Values (in cm^{-1}) for the FWHM are shown below for a pressure of 1 atm. While Doppler broadening may be neglected at 300 K, it clearly cannot be neglected at 2000 K.

T [K]	$\Delta \nu_C$	$\Delta \nu_D$
300	0.12	0.004
2000	0.05	0.01

Sodium, Na

A narrowband laser is tuned to the linecenter of the 589 nm sodium transition. It is used to infer the partial pressure of sodium which is seeded into an atmospheric pressure flame. The temperature has been determined to be 1600 K. The partial pressure is obtained from a linecenter absorption measurement via the absorption coefficient. First, solve for k_{ν_0} from the measured fractional transmission at linecenter; next, evaluate the linecenter value of the lineshape function; finally, solve for P_i using the known value for the line strength at 1600 K.

(1) find $k_{\nu_0} = (-1/L) \ln(I/I^0)_{\nu_0}$
(2) find $\phi(\nu_0)$
(3) find P_i using Eq. (8.48)

$$P_i = \frac{k_\nu}{S\phi(\nu_0)} \tag{8.48}$$

To evaluate $\phi(\nu_0)$, first calculate the collisional and Doppler halfwidths. Assume that the collisional broadening is adequately characterized by collisions with N_2, the major species in an air flame:

$$\Delta \nu_C = P \cdot 2\gamma(1600\,\text{K}) = P \cdot 2\gamma(300\,\text{K})\sqrt{\frac{300}{1600}} = 0.21\,\text{cm}^{-1}$$

This example uses the value of 2γ at 300 K (see Table 8.1) and scales it to 1600 K. Next, convert the wavelength to frequency:

$$(589 \times 10^{-7}\,\text{cm})^{-1} = 16,978\,\text{cm}^{-1}$$

and calculate the Doppler halfwidth with Eq. (8.24):

$$\Delta \nu_D = (7.17 \times 10^{-7})(16,978 \, \text{cm}^{-1}) \left(\frac{1600}{23} \right)^{1/2} = 0.10 \, \text{cm}^{-1}$$

Next, calculate the Voigt a parameter with Eq. (8.30):

$$a = \frac{\sqrt{\ln 2} \, \Delta \nu_C}{\Delta \nu_D} = \frac{\sqrt{\ln 2} \, (0.21)}{0.10} = 1.75$$

Using the Voigt tables, interpolate between $a = 1.70$ and 1.80 for $w = 0$ (linecenter) to get $V(a, w) = V(1.75, 0) = 0.2852$. Calculate $\phi_D(\nu_o)$ from Eq. (8.32):

$$\phi_D(\nu_o) = \frac{2}{\Delta \nu_D} \sqrt{\frac{\ln 2}{\pi}} = \frac{2}{0.10} \sqrt{\frac{\ln 2}{\pi}} = 9.39 \, \text{cm}$$

The lineshape function can now be found from Eq. (8.35):

$$\phi(\nu_o) = \phi_D(\nu_o) \, V(0) = 9.39 \times 0.2852 = 2.68 \, \text{cm}$$

Now solve for P_i using Eq. (8.48). Note that $S(T)$ can be calculated from Einstein coefficients or the oscillator strength, if $S(T)$ is not already known (see Chap. 7).

Atomic H Velocity
LIF (Laser Induced Fluorescence) in an arcjet thruster is used to measure the Doppler shift of atomic hydrogen at 656 nm. The laser is directed into the flow in an axial direction (relative to the arcjet), and a shift of $0.70 \, \text{cm}^{-1}$ is observed. The corresponding velocity component is found by using Eq. (8.40):

$$u = \frac{c \, \delta \nu}{\nu_0} = \frac{3 \times 10^8 \, \text{m/s} \times 0.70 \, \text{cm}^{-1}}{15,232 \, \text{cm}^{-1}} = 13,800 \, \text{m/s}$$

8.7 Exercises

1. Neglecting all broadening mechanisms except collision and Doppler broadening, write a general expression for the Voigt a parameter of a single gas system, in terms of the total pressure, temperature, optical collision diameter (σ), and the transition center frequency.
2. Given a sample cell filled with pure $^{12}\text{C}^{16}\text{O}$ at atmospheric pressure and $\sigma = 4.0 \, \text{Å}$, determine at what temperature $a = \sqrt{\ln 2}$ for $\bar{\nu}_0 = 2100 \, \text{cm}^{-1}$ (an IR transition) and for $\bar{\nu}_0 = 22,170 \, \text{cm}^{-1}$ (a visible transition).
3. For $T = 300 \, \text{K}$, $\sigma = 4.0 \, \text{Å}$, and a line strength $S = 10 \, \text{cm}^{-2} \, \text{atm}^{-1}$, plot the spectral absorption coefficient at line center, $\beta(\bar{\nu}_0) \, \text{cm}^{-1}/\text{atm}$, versus pressure from 0 to 3 atmospheres, for the $2100 \, \text{cm}^{-1}$ transition.

4. What atmospheric path length, L (cm), is required at 300 K, 1 atm total pressure, to give 60 % absorption at the center of this transition when CO is present at a level of 10 ppm in the atmosphere? You may neglect the small differences in mass between CO, O_2, and N_2. You may also assume that the optical collision diameters for CO, O_2, and N_2 are equal.

5. A pure gas of molecular weight 25 g/mole is at $T = 300$ K, and $P = 1$ atm. The rovibronic transition at $\lambda = 700$ nm is characterized by a Voigt a parameter $a = 0.5$. Determine the new Voigt a parameter value at $T = 600$ K and $P = 4$ atm. You may assume that the optical collision diameter is invariant with temperature.

   Hints for these problems:

   (a) In order to eliminate interpolation of the Voigt tables you may choose to pick values of P that correspond to convenient values of a. In other words, select a value of a, then calculate the corresponding value of P.

   (b) For $a > 10$, the effect of Doppler broadening is small and purely Lorentzian lineshape may be assumed.

   (c) Use a semi-log plot ($\log \beta$ vs. P) to more clearly display the wide variations in $\beta(\overline{\nu}_0)$.

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