# Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

## Lecture 6: Spectral Lineshapes

1. Background introduction
2. Types of line broadening
3. Voigt profiles
4. Uses of quantitative lineshape measurements
5. Working examples

A typical lineshape function

# 1. Background introduction

- Beer's Law

Recall:

absorption coefficient @ $\nu$, $cm^{-1}$

$$T_\nu = (I / I_0)_\nu = I_\nu / I_\nu^0 = \exp(-k_\nu L)$$

intensity or power @ $\nu$ spectral intensity @ $\nu$

$$\boxed{k_\nu, \mathrm{cm}^{-1} = S_{12}\left[\mathrm{cm}^{-1}\cdot\mathrm{s}^{-1}\right]\phi[\mathrm{s}]}$$

Line strength, $\int_{line} k_\nu d\nu$

$$\boxed{\phi(\nu) = \frac{k_\nu}{\int_{line} k_\nu d\nu}, \int_{-\infty}^{\infty}\phi(\nu)d\nu = 1}$$

$$S_{12}\left[\mathrm{cm}^{-1}\cdot\mathrm{s}^{-1}\right] = \left(\frac{h\nu}{c}\right) n_1 B_{12}\left(1-\exp(-h\nu/kT)\right)$$

$$= \frac{\lambda^2}{8\pi} n_1 A_{21}\left(\frac{g_2}{g_1}\right)\left(1-\exp(-h\nu/kT)\right)$$

← **The lineshape function**

# 1. Background introduction

- Alternate forms of $\nu$, $\phi$, $S_{12}$
  - $\nu$ $\quad \nu, \mathrm{s}^{-1} = \frac{c}{\lambda} = c\left(\bar{\nu}, \mathrm{cm}^{-1}\right)$
  - $\phi$ $\quad \phi, \mathrm{cm} = c(\phi, \mathrm{s})$
  - $S_{12}$
    - A common form of S

      $$S_{12}, \mathrm{cm}^{-2} = \left(S_{12}, \mathrm{cm}^{-1}\mathrm{s}^{-1}\right)/c$$

    - Another common form

      $$S_{12}, \mathrm{cm}^{-2}/\mathrm{atm} = \left(S_{12}, \mathrm{cm}^{-2}\right)/\left(P_i, \mathrm{atm}\right) = \frac{S_{12},\ \mathrm{cm}^{-1}\,\mathrm{s}^{-1}}{cP_i, \mathrm{atm}}$$

      Partial pressure of absorber

$$k_\nu, \mathrm{cm}^{-1} = S_{12}\left[\mathrm{cm}^{-1}\cdot\mathrm{s}^{-1}\right]\phi[\mathrm{s}]$$

or

$$k_\nu, \mathrm{cm}^{-1} = S_{12}\,[\mathrm{cm}^{-2}]\,\phi\,[\mathrm{cm}]$$

✎Notes:

1. $$\frac{n_1}{P_i, \mathrm{atm}} = \frac{n_1}{n_i kT/1.013\times10^6\,\mathrm{dynes/cm^2atm}} = \frac{1}{kT}\left(\frac{n_1}{n_i}\right)10^6$$

   ← Boltzmann fraction

2. $$k_\nu, \mathrm{cm}^{-1} = \left(S_{12}, \mathrm{cm}^{-2}/\mathrm{atm}\right)\left(P_i, \mathrm{atm}\right)\left(\phi, \mathrm{cm}\right)$$

   $$P_i, \mathrm{atm} = \left(P, \mathrm{atm}\right)\left(\chi_i\right)$$

   ← Mole fraction

$$= \frac{c}{8\pi\nu^2}\frac{n_1}{P_i, \mathrm{atm}}A_{21}\frac{g_2}{g_1}\left(1-\exp\left(-h\nu/kT\right)\right)$$

- $$\left(S_{12}, \mathrm{cm}^{-2}\mathrm{atm}^{-1}\right)\left(P_i, \mathrm{atm}\right) = \left(S^*, \frac{\mathrm{cm}^{-1}}{\mathrm{molec/cm^2}}\right)\left(n_i, \frac{\mathrm{molec}}{\mathrm{cm}^3}\right)$$

  HITRAN database lists S* (cm/molec), usually at $T_{ref}$ = 296K

# 1. Background introduction

- How are $S_{12}$ and $\phi$ measured?

➡ High-resolution absorption experiments

$$\phi = \frac{k_\nu}{\int_{\text{line}} k_\nu \, d\nu}$$

- Area=1
- Shape determined by main broadening mechanisms

# 2. Types of line broadening

- Brief overview

| | |
|---|---|
| Lorentzian<br>Homogeneous (affects all molecules equally) | 1. Natural broadening<br>➡ Result of finite radiative lifetime<br>2. Collisional/pressure broadening<br>➡ Finite lifetime in quantum state owing to collisions |
| Gaussian<br>Inhomogeneous (affects certain class of molecule) | 3. Doppler broadening<br>➡ Thermal motion |
| Lorentzian + Gaussian | 4. Voigt profile<br>➡ Convolution of 1-3 |

# 2. Types of line broadening

- Natural line broadening

1. Heisenberg uncertainty principle: $\Delta E_u \Delta t_u \geq h/2\pi$

$\Delta E_u$ = uncertainty in energy of $u$

$\Delta t_u = \tau$, the uncertainty in time of occupation of $u$

$\Delta E_u = h\Delta\nu_u = (h/2\pi)/(\Delta t = \tau_{rad})$ ➡ $\boxed{\Delta\nu_u = 1/2\pi\tau_{rad}}$ "lifetime" limited

2. In general

$$\Delta\nu_N = \Delta\nu_u + \Delta\nu_l = \frac{1}{2\pi}\left(\frac{1}{\tau_u} + \cancel{\frac{1}{\tau_l}}\right)$$

0 for ground state (natural broadening)

# 2. Types of line broadening

- Natural line broadening

3. Typical values
   - Electronic transitions:

$$\tau_u \sim 10^{-8}\,\mathrm{s} \rightarrow \Delta\nu_N \sim 1.6\times10^{7}\,\mathrm{s}^{-1}$$

$$\Delta\omega_N, \mathrm{cm}^{-1} = \Delta\nu_N / c = 5\times10^{-4}\,\mathrm{cm}^{-1}$$

   - Vib-rot transitions

$$\tau_u \sim 10^{-2}\,\mathrm{s} \rightarrow \Delta\nu_N \sim 16\,\mathrm{s}^{-1}, \Delta\omega_N, \mathrm{cm}^{-1} = 5\times10^{-10}\,\mathrm{cm}^{-1}$$

   - These are typically much smaller than $\Delta\nu_D$ and $\Delta\nu_C$

4. Lineshape function – "Lorentzian" – follows from Fourier transform

$$\phi(\nu)_N = \frac{1}{\pi}\frac{\Delta\nu_N/2}{(\nu-\nu_0)^2 + (\Delta\nu_N/2)^2}$$

Note: a) $\phi_{\max} = \phi(\nu_0) = \frac{2}{\pi}\frac{1}{\Delta\nu_N}$

b) $\phi(\nu - \nu_0 = \Delta\nu_N/2) = \phi(\nu_0)/2$

# 2. Types of line broadening

- Natural line broadening

Lineshape derivation from damped oscillator model (Ref. Demtröder)

$\gamma$ = Damping ratio
$\gamma = \Delta\nu_n \sim 1/\Delta\tau \cdot 2\pi$
in units of $s^{-1}$

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = 0,\ \ \omega_0^2 = k/m$$
$$x(0) = x_0, \dot{x}(0) = 0$$

$$x(t) = x_0 \exp(-\gamma t/2)\left[\cos\omega t + (\gamma/2\omega)\sin\omega t\right]$$
$$\omega = \left(\omega_0^2 - \gamma^2/4\right)^{1/2}$$

Small damping ($\gamma << \omega_0$)

$$x(t) = x_0 \exp(-\gamma t/2)\cos\omega_0 t$$

Amplitude of x(t) decrease ➡ frequency of emitted radiation is no longer monochromatic

$$x(t) = \frac{1}{2\sqrt{2\pi}}\int_0^\infty A(\omega)\exp(i\omega t)d\omega$$

$$A(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^\infty x(t)\exp(-i\omega t)dt$$

$$= \frac{x_0}{\sqrt{8\pi}}\left(\frac{1}{i(\omega-\omega_0)+\gamma/2} + \frac{1}{i(\omega+\omega_0)+\gamma/2}\right)$$

$$I(\omega) \propto A(\omega)A^*(\omega), L = I/I_0$$

$$L(\omega-\omega_0) = \frac{1}{\pi}\frac{\gamma/2}{(\omega-\omega_0)^2 + (\gamma/2)^2}$$

# 2. Types of line broadening

- Collision broadening
  1. Also lifetime limited – time set by collision time interval

$Z_{BA}$ = # collision/s of a single B with all A

#/cc

$$= n_A \cdot \pi\sigma_{AB}^2 \cdot \left( \bar{c} = \sqrt{\frac{8kT}{\pi\mu_{AB}}} \right)$$

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

For a mixture,

$$Z_B = \sum_A n_A \cdot \pi\sigma_{AB}^2 \cdot \sqrt{\frac{8kT}{\pi\mu_{AB}}}$$

$$= P\sum_A X_A \cdot \pi\sigma_{AB}^2 \cdot \sqrt{\frac{8}{\pi\mu_{AB}kT}}$$

$$P, \text{dynes/cm}^2 = 1.013\times10^6 (P, \text{atm})$$

# 2. Types of line broadening

- Collision broadening
  1. Also lifetime limited – time set by collision time interval

$$Z_B = \sum_A n_A \cdot \pi\sigma_{AB}^2 \cdot \sqrt{\frac{8kT}{\pi\mu_{AB}}} = P\sum_A X_A \cdot \pi\sigma_{AB}^2 \cdot \sqrt{\frac{8}{\pi\mu_{AB}kT}}$$

Since

$$\Delta\nu_C, \mathrm{s}^{-1} = \frac{1}{2\pi}\left(\frac{1}{\tau_{coll,upper}} + \frac{1}{\tau_{coll,lower}}\right) \cong \frac{Z_B}{\pi}$$

$$= (P, \mathrm{atm})\sum_A X_A \cdot \underbrace{\sigma_{AB}^2 \cdot \sqrt{\frac{8}{\pi\mu_{AB}kT}} \cdot 1.013\times10^6}_{2\gamma_A, \mathrm{s}^{-1}/\mathrm{atm}}$$

$$\Delta\nu_C, \mathrm{s}^{-1} = (P, \mathrm{atm})\sum_A X_A 2\gamma_A$$

$2\gamma_A$ = collison halfwidth, i.e., FWHM per atm pressure

Notes:

$$\Delta\nu_C, \mathrm{cm}^{-1} = \Delta\nu_C, \mathrm{s}^{-1}/c$$

$$2\gamma, \mathrm{cm}^{-1}/\mathrm{atm} = 2\gamma, \mathrm{s}^{-1}/\mathrm{atm}/c$$

2. Lineshape function – Lorentzian $\phi(\nu)_{coll} = \frac{1}{\pi}\frac{\Delta\nu_C/2}{(\nu-\nu_0)^2 + (\Delta\nu_C/2)^2}$

3. Crude approximation $2\gamma(T) = \underbrace{2\gamma^{300}}_{\approx 0.1\,\mathrm{cm}^{-1}/\mathrm{atm}}(300/T)^n$ ← n=1/2 for hard sphere

cm$^{-1}$/atm

# 2. Types of line broadening

- Collision broadening

$$\Delta\nu_C, \mathrm{cm}^{-1} = (P, \mathrm{atm})\sum_A X_A 2\gamma_A$$

with $2\gamma_A$ in $\mathrm{cm}^{-1}/\mathrm{atm}$

Example: Pressure broadening of CO

R(9) line of CO's 2nd overtone, 50ppm in Air, 300K, 1.0atm
Species population: 77% $N_2$, 20% $O_2$, 2% $H_2O$ (85% humidity) 380ppm $CO_2$

| Species, A | Mole Fraction, $X_A$ | $2\gamma_{CO\text{-}A}$ (300K) $\mathrm{cm}^{-1}/\mathrm{atm}$ |
|---|---|---|
| $N_2$ | 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 |

$$\begin{aligned}\Delta\nu_C &= P\big(X_{N_2}\cdot 2\gamma_{CO-N_2} + X_{H_2O}\cdot 2\gamma_{H_2O-N_2} + X_{CO}\cdot 2\gamma_{CO-CO} \\ &\quad + X_{CO_2}\cdot 2\gamma_{CO-CO_2} + X_{O_2}\cdot 2\gamma_{CO-O_2}\big) \\ &= 0.115\mathrm{cm}^{-1}\end{aligned}$$

# 2. Types of line broadening

- Collision broadening

Some collisional broadening coefficients 2γ [$cm^{-1}$/atm] in Ar and $N_2$ at 300K

| 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 |

Some collisional broadening coefficients 2γ [$cm^{-1}$/atm] in Ar and $N_2$ at 2000K

| Species | Wavelength [nm] | Ar | $N_2$ |
|---|---|---|---|
| NO | 225 | 0.14 | 0.14 |
| OH | 306 | 0.034 | 0.04 |
| NH | 335 | 0.038 | |

# 2. Types of line broadening

- Doppler broadening

1. Moving molecules see different frequency (Doppler shift)

$$\left|\nu_{app} - \nu_{act}\right| = \nu_{act} u / c = u / \lambda \Rightarrow \nu_{app} = \nu_{act}\left(1 - u / c\right)$$

molec. velocity along beam path

2. Gaussian velocity distribution function (leads to Gaussian $\phi(\nu)$)

$$\phi(\nu) = \underbrace{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D}}_{\phi(\nu_0)} \exp\left[-\left(\frac{2\sqrt{\ln 2}}{\Delta\nu_D}(\nu - \nu_0)\right)^2\right]$$

$$\Delta\nu_D(\mathrm{FWHM}) = 2\sqrt{\frac{2kT\ln 2}{mc^2}}\nu_0$$

$$\Delta\nu_D(\mathrm{FWHM}) = 7.17 \times 10^{-7}\nu_0\sqrt{\frac{T}{M}}$$

g/mole of emitter/absorber

- Aside:

Maxwellian velocity distribution

$$f(U_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mU_x^2}{2kT}\right)$$

# 2. Types of line broadening

- Stark broadening
  - Important in charged gases, i.e., plasmas
  - Coulomb forces perturb energy levels
- Types of instrument broadening
  - Instruments have insufficient resolution
  - Powerful lasers can perturb populations away from equilibrium (saturation effect)
- Another type of lifetime-limited broadening is transit-time broadening

$$\text{Transit time} \approx D / V$$

$$\therefore \Delta\nu_{transit} \approx V / D$$

for apparent broadening of an abs. line

Reference: Demtröder p.85-p.88

# 2. Types of line broadening

- Examples

1st Example:

T = 300K, M = 30g/mole, P = 1atm

- Electronic transition ($\lambda$=600nm, v=5x10$^{14}$s$^{-1}$)

$$\Delta\nu_D = 1.1\times10^9\,\mathrm{s}^{-1} \sim 0.04\,\mathrm{cm}^{-1}$$

$$\Delta\nu_D >> \Delta\nu_N \sim 10^7\,\mathrm{s}^{-1}$$

$$\Delta\nu_C \sim 3\times10^9\,\mathrm{s}^{-1} = 0.1\,\mathrm{cm}^{-1}$$

$$\therefore \Delta\nu_D < \Delta\nu_C$$

- Vib-rot transition ($\lambda$=6μm, v=5x10$^{13}$s$^{-1}$)

→ $\lambda_{IR}=10\lambda_{vis}$

$$\Delta\nu_D \sim 1.1\times10^8\,\mathrm{s}^{-1} \sim 0.004\,\mathrm{cm}^{-1}$$

$$\Delta\nu_C \sim 3\times10^9\,\mathrm{s}^{-1} = 0.1\,\mathrm{cm}^{-1}$$

$$\therefore \Delta\nu_D << \Delta\nu_C$$

2nd Example:

T = 2700K, M = 30g/mole, P = 1atm

- Electronic transition ($\lambda$=600nm, v=5x10$^{14}$s$^{-1}$)

$$\underbrace{\Delta\nu_D}_{\sim T^{1/2}} \sim 0.11\,\mathrm{cm}^{-1} > \underbrace{\Delta\nu_C}_{\sim T^{-1/2}} \sim 0.03\,\mathrm{cm}^{-1}$$

- Vib-rot transition ($\lambda$=6μm, v=5x10$^{13}$s$^{-1}$)

$$\Delta\nu_D \sim 0.01\,\mathrm{cm}^{-1} < \Delta\nu_C \sim 0.03\,\mathrm{cm}^{-1}$$

# 2. Types of line broadening

- Conclusions
  - Doppler broadening most significant at:

    Low P, high T, small λ

  - Collision broadening most significant at:

    High P, low T, large λ

  - Many conditions require consideration of both effects

    Together ➡ Voigt profile!

# 3. Voigt Profiles

1. Dominant types of broadening
   - Collision broadening
   - Doppler broadening
2. Voigt profile
3. Line-shifting mechanisms

# 3. Voigt profiles
## 3.1. Dominant types of broadening

- Collision broadening review
  - $\phi_C(\nu) = \frac{1}{\pi} \frac{\Delta\nu_C/2}{(\nu-\nu_0)^2 + (\Delta\nu_C/2)^2}$ Lorentzian form "lifetime limited"
  - $\Delta\nu_C, \mathrm{s}^{-1} = \left(\sum_A X_A 2\gamma_A\right)(P, \text{atm of mixture})$

    mole fraction of A — coll. width/atm for A as coll. partner, $\propto \sqrt{1/T}$
  - Typical value of $2\gamma_A$ ~ 0.1cm$^{-1}$/atm (or 0.3x10$^{10}$s$^{-1}$/atm)

    - Aside: $2\gamma_A, \mathrm{s}^{-1} = \frac{1}{c} 1.013\times10^6 \sigma_{AB}^2 \cdot \sqrt{\frac{8}{\pi\mu_{AB}kT}} \propto \sqrt{\frac{1}{T}}$

      if $\sigma_{AB}$ is constant

      $0.1\mathrm{cm}^{-1}/\mathrm{atm} \cdot 3\times10^{10}\mathrm{cm/s} = 0.3\times10^{10}\mathrm{s}^{-1}/\mathrm{atm}$
  - A type of "Homogenous broadening", i.e., same for all molecules of absorbing species

# 3. Voigt profiles
## 3.1. Dominant types of broadening

- Doppler broadening review
  - $$\phi(\nu) = \underbrace{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D}}_{\phi(\nu_0)} \exp\left[-\left(\frac{2\sqrt{\ln 2}}{\Delta\nu_D}(\nu-\nu_0)\right)^2\right]$$ Gaussian form
  - $$\Delta\nu_D, \mathrm{s}^{-1} = 2\left(\frac{2kT\ln 2}{mc^2}\right)^{1/2}\nu_0 = 7.17\times10^{-7}\nu_0\sqrt{T/M}$$

    FWHM

    g/mole of absorber/emitter
  - Typical value

    $$\Delta\nu_D(\lambda = 600\mathrm{nm}, M = 30) = 0.35\times10^{10}\,\mathrm{s}^{-1}(3000\mathrm{K}) \approx 0.12\mathrm{cm}^{-1}$$
    $$= 0.1\times10^{10}\,\mathrm{s}^{-1}(300\mathrm{K}) \approx 0.03\mathrm{cm}^{-1}$$
  - This is a type of “Inhomogenous broadening”, i.e., depends on specific velocity class of molecule

# 3. Voigt profiles
## 3.1. Dominant types of broadening

- Comparison of $\phi_D$ and $\phi_C$ (for same $\Delta\nu$(FWHM))

- Both have same area (unity)
- Peak heights

$$\phi(\nu_0)_{Dopp} = \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D} = 0.94/\Delta\nu_D$$

$$\phi(\nu_0)_{coll} = \frac{2}{\pi}\frac{1}{\Delta\nu_C} = 0.637/\Delta\nu_C$$

➡ for $\Delta\nu_C/\Delta\nu_D = 1$

$$\phi(\nu_0)_{Dopp} = 1.48\phi(\nu_0)_{coll}$$

- Gaussian: higher near peak
- Lorentzian: higher in wings

- Some exceptions/improved models
  - Collision narrowing (low-pressure phenomenon)
    ➡ Galatry profiles, others, with additional parameters
  - Stark broadening ➡ Plasma phenomenon

*Ready to combine Doppler & collision broadening; done via Voigt profile*

# 3.2. Voigt profile

- Physical argument

The physical argument employed in establishing the Voigt profile is that the effects of Doppler & collision broadening are decoupled. Thus we argue that every point on a collision-broadened lineshape is further broadened by Doppler effects.

Convolution: $\phi_V(\nu) = \phi_D(\nu) * \phi_C(\nu) = \int_{-\infty}^{\infty} \phi_D(u)\phi_C(\nu - u)du$

$$\Rightarrow \phi_V(\nu) = \int_{-\infty}^{\infty} \left[ \frac{1}{\pi} \frac{\Delta\nu_C/2}{(\Delta\nu_C/2)^2 + (\nu - \nu_0 - \delta)^2} \right] \left[ \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D} \exp\left[ -\left( \frac{2\sqrt{\ln 2}}{\Delta\nu_D}\delta \right)^2 \right] \right] d\delta$$

$$\Rightarrow \boxed{\phi_V(\nu) = \underbrace{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D}}_{\phi_D(0)} \left\{ \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-y^2)dy}{a^2 + (w-y)^2} \equiv V(a,w) \right\}}$$

the "Voigt function" (V≤1)

where $a = \sqrt{\ln 2}(\Delta\nu = \Delta\nu_C + \Delta\nu_N)/\Delta\nu_D \approx \sqrt{\ln 2}\Delta\nu_C/\Delta\nu_D$

$w = 2\sqrt{\ln 2}(\nu - \nu_0)/\Delta\nu_D$

$y = 2\delta\sqrt{\ln 2}/\Delta\nu_D$ (integrated out)

# 3.2. Voigt profile

$$\phi_V(\nu) = \underbrace{\left\{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D}\right\}}_{\phi_D(0)} \left\{\frac{a}{\pi}\int_{-\infty}^{\infty}\frac{\exp\left(-y^2\right)dy}{a^2+(w-y)^2} \equiv V(a,w)\right\}$$

the "Voigt function" (V≤1)

✐Notes:

1. $\phi_V(\nu) = \phi_D(\nu_0)V(a,w)$, so that
2. $k_\nu = k_0 V(a,w)$

Spec. abs. coeff.

$k_D(\nu_0)$, the line-center spec. abs. coeff. for Doppler broadening

Recall: $k_\nu = S\phi$

3. $V(a,0) = \exp\left(a^2\right)\mathrm{erfc}(a)$

$\therefore \phi_V(\nu_0) = \phi_D(\nu_0)\cdot\exp\left(a^2\right)\mathrm{erfc}(a)$

$w = 2\sqrt{\ln 2}(\nu-\nu_0)/\Delta\nu_D$

***a***=1: $\exp\left(a^2\right)\mathrm{erfc}(a) = 0.43$

***a***=2: $\exp\left(a^2\right)\mathrm{erfc}(a) = 0.257$

# 3.2. Voigt profile

- Voigt table

| $w \backslash a$ | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.80 | 0.90 | 1.00 |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.00 | 0.8965 | 0.8090 | 0.7346 | 0.6708 | 0.6157 | 0.5678 | 0.5259 | 0.4891 | 0.4565 | 0.4276 |
| 0.10 | 0.8885 | 0.8026 | 0.7293 | 0.6665 | 0.6121 | 0.5648 | 0.5234 | 0.4870 | 0.4547 | 0.4260 |
| 0.20 | 0.8650 | 0.7835 | 0.7138 | 0.6537 | 0.6015 | 0.5560 | 0.5160 | 0.4807 | 0.4494 | 0.4215 |
| 0.30 | 0.8272 | 0.7529 | 0.6887 | 0.6330 | 0.5843 | 0.5416 | 0.5039 | 0.4705 | 0.4407 | 0.4140 |
| 0.40 | 0.7773 | 0.7121 | 0.6552 | 0.6053 | 0.5613 | 0.5222 | 0.4876 | 0.4566 | 0.4288 | 0.4038 |
| 0.50 | 0.7176 | 0.6632 | 0.6149 | 0.5717 | 0.5332 | 0.4986 | 0.4675 | 0.4395 | 0.4142 | 0.3912 |
| 0.60 | 0.6511 | 0.6083 | 0.5692 | 0.5336 | 0.5011 | 0.4715 | 0.4444 | 0.4198 | 0.3972 | 0.3766 |
| 0.70 | 0.5807 | 0.5497 | 0.5202 | 0.4923 | 0.4661 | 0.4417 | 0.4190 | 0.3979 | 0.3783 | 0.3602 |
| 0.80 | 0.5093 | 0.4897 | 0.4695 | 0.4492 | 0.4294 | 0.4103 | 0.3919 | 0.3745 | 0.3580 | 0.3425 |
| 0.90 | 0.4394 | 0.4303 | 0.4187 | 0.4058 | 0.3920 | 0.3780 | 0.3640 | 0.3502 | 0.3368 | 0.3239 |
| 1.00 | 0.3732 | 0.3732 | 0.3694 | 0.3630 | 0.3549 | 0.3456 | 0.3357 | 0.3254 | 0.3151 | 0.3047 |
| 1.20 | 0.2574 | 0.2709 | 0.2792 | 0.2834 | 0.2846 | 0.2835 | 0.2807 | 0.2767 | 0.2718 | 0.2662 |
| 1.40 | 0.1684 | 0.1892 | 0.2047 | 0.2157 | 0.2233 | 0.2280 | 0.2306 | 0.2314 | 0.2308 | 0.2292 |
| 1.60 | 0.1058 | 0.1289 | 0.1473 | 0.1617 | 0.1728 | 0.1812 | 0.1872 | 0.1914 | 0.1940 | 0.1954 |
| 1.80 | 0.0651 | 0.0871 | 0.1055 | 0.1208 | 0.1333 | 0.1434 | 0.1514 | 0.1576 | 0.1623 | 0.1657 |
| 2.00 | 0.0402 | 0.0595 | 0.0764 | 0.0909 | 0.1034 | 0.1138 | 0.1226 | 0.1298 | 0.1356 | 0.1402 |
| 2.20 | 0.0257 | 0.0419 | 0.0566 | 0.0697 | 0.0812 | 0.0912 | 0.0999 | 0.1074 | 0.1137 | 0.1189 |
| 2.40 | 0.0174 | 0.0308 | 0.0432 | 0.0546 | 0.0649 | 0.0741 | 0.0823 | 0.0896 | 0.0959 | 0.1013 |
| 2.60 | 0.0126 | 0.0237 | 0.0341 | 0.0438 | 0.0529 | 0.0612 | 0.0687 | 0.0755 | 0.0815 | 0.0869 |
| 2.80 | 0.0098 | 0.0189 | 0.0277 | 0.0361 | 0.0439 | 0.0513 | 0.0580 | 0.0643 | 0.0699 | 0.0750 |
| 3.00 | 0.0079 | 0.0156 | 0.0231 | 0.0303 | 0.0371 | 0.0436 | 0.0497 | 0.0553 | 0.0605 | 0.0653 |

# 3.2. Voigt profile

- Procedure
  - Given: T, M, $\nu_0$, P, σ, or 2γ
  - Desire: $\phi(\nu)$

$$\phi_V(\nu) = \underbrace{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D}}_{\phi_D(0)} \left\{ \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-y^2)dy}{a^2 + (w-y)^2} \equiv V(a,w) \right\}$$

the "Voigt function" (V≤1)

1. Compute: $\Delta\nu_D$ and $\phi_D(\nu_0)$
2. Compute: $\Delta\nu_C$
3. Compute: $a = \sqrt{\ln 2}\Delta\nu_C / \Delta\nu_D$
4. Pick w, enter table (for $a$) and obtain $k_\nu / k_D(\nu_0) = \phi / \phi_D(\nu_0)$
5. Solve for $\nu - \nu_0$ (and hence $\nu$) for that w
6. Results: $\phi(\nu)$ vs $\nu - \nu_0$

| $w \backslash a$ | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.80 | 0.90 | 1.00 |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.00 | 0.8965 | 0.8090 | 0.7346 | 0.6708 | 0.6157 | 0.5678 | 0.5259 | 0.4891 | 0.4565 | 0.4276 |
| 0.10 | 0.8885 | 0.8026 | 0.7293 | 0.6665 | 0.6121 | 0.5648 | 0.5234 | 0.4870 | 0.4547 | 0.4260 |
| 0.20 | 0.8650 | 0.7835 | 0.7138 | 0.6537 | 0.6015 | 0.5560 | 0.5160 | 0.4807 | 0.4494 | 0.4215 |
| 0.30 | 0.8272 | 0.7529 | 0.6887 | 0.6330 | 0.5843 | 0.5416 | 0.5039 | 0.4705 | 0.4407 | 0.4140 |
| 0.40 | 0.7773 | 0.7121 | 0.6552 | 0.6053 | 0.5613 | 0.5222 | 0.4876 | 0.4566 | 0.4288 | 0.4038 |
| 0.50 | 0.7176 | 0.6632 | 0.6149 | 0.5717 | 0.5332 | 0.4986 | 0.4675 | 0.4395 | 0.4142 | 0.3912 |

# 3.2. Voigt profile

- Procedure
  - Given: T, M, $\nu_0$, P, σ, or 2γ
  - Desire: $\phi(\nu)$

$$\phi_V(\nu) = \underbrace{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D}}_{\phi_D(0)} \left\{ \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-y^2)dy}{a^2 + (w-y)^2} \equiv V(a,w) \right\}$$

the "Voigt function" (V≤1)

1. Compute: $\Delta\nu_D$ and $\phi_D(\nu_0)$
2. Compute: $\Delta\nu_C$
3. Compute: $a = \sqrt{\ln 2}\Delta\nu_C / \Delta\nu_D$
4. Pick w, enter table (for $a$) and obtain $k_\nu / k_D(\nu_0) = \phi / \phi_D(\nu_0)$
5. Solve for $\nu - \nu_0$ (and hence $\nu$) for that w
6. Results: $\phi(\nu)$ vs $\nu - \nu_0$

- Refinements
  - Galatry profiles (collision narrowing)
  - Berman profiles (speed-dependent broadening)

# 3. Voigt profiles
# 3.3. Line-shifting mechanisms

- Pressure shift of absorption lines
  - Interaction between two collision partners can have a perturbing effect on the intermolecular potential of the molecule
    - ➡ leads to differences in the energy level spacings
    - ➡ leads to pressure shift

$$\Delta\nu_S = P\sum_A X_A \delta_A$$

$\delta_A$: cm$^{-1}$/atm

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

✐Notes:

1. While 2γ>0, δ can be + or –
2. E.g., average values for IR $H_2O$ spectra: δ = –0.017cm$^{-1}$/atm, M=0.96

- Doppler shift

$$\delta\nu = \nu_0(u/c)$$

# 4. Uses of quantitative lineshape measurements

- Species concentration and pressure
  - Integrated absorbance area

$$A_i = \int_{-\infty}^{\infty} \alpha(\nu) d\nu = S_i P X_j L$$

Line strength of the transition — Pressure — Species mole fraction — Pathlength

$$\Rightarrow X_j = \frac{A_i}{S_i P L}$$

$$\Rightarrow P = \frac{A_i}{S_i X_j L}$$

- Temperature
  - FWHM of lineshape gives T in Doppler-limited applications
  - Two-line technique with non-negligible pressure broadening

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

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

T sensitivity:

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

Large ΔE" for higher sensitivity;
Absorbance: 0.1<α<2.3
➡ Tradeoff between acceptable absorbance and T sensitivity.

# 4. Uses of quantitative lineshape measurements

- Examples

- 1st Example: Spectrally resolved absorption of sodium (Na) in a heated cell

λ = 589nm, T = 1600K, P = 1atm

*What is $P_{Na}$?*

1) Find $k_{\nu_0} = (-1/L)\ln(I/I^0)_{\nu_0}$
2) Find $\phi(\nu_0)$
3) Find $P_i$

$$\Delta\nu_C = P\cdot 2\gamma(1600\text{K})$$

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

$$(589\times10^{-7}\text{cm})^{-1} = 16978\text{cm}^{-1}$$

$$\Delta\nu_D = (7.17\times10^{-7})(16978\text{cm}^{-1})\left(\frac{1600}{23}\right)^{1/2}$$

$$= 0.10\text{cm}^{-1}$$

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

Interpolate Voigt table

$$V(a,w) = V(1.75,0) = 0.2852$$

$$\phi_D(\nu_0) = \frac{2}{\Delta\nu_D}\sqrt{\frac{\ln 2}{\pi}} = \frac{2}{0.10}\sqrt{\frac{\ln 2}{\pi}} = 9.39\text{cm}$$

$$\phi(\nu_0) = \phi_D(\nu_0)V(0)$$

$$= 9.39\times0.2852 = 2.68\text{cm}$$

Solve for $P_i$ using $P_i = \dfrac{k_\nu}{S\phi(\nu_0)}$

Also could solve for T from lineshape data

* $2\gamma(300\text{K}) = 0.49\text{cm}^{-1}$ from slide 12

# 4. Uses of quantitative lineshape measurements

- Examples
  - 2nd Example: Atomic H velocity

LIF (Laser Induced Fluorescence) in an arcjet thruster is used to measure the Doppler shift of atomic hydrogen at 656nm.

Doppler shift: $\delta\nu = 0.70\text{cm}^{-1}$

Use line position to infer velocity

The corresponding velocity component is found

$$u = \frac{c\delta\nu}{\nu_0} = \frac{3\times10^8\,\text{m/s}\times0.70\text{cm}^{-1}}{15{,}232\text{cm}^{-1}} = 13800\text{m/s}$$

# 5. Working examples - 1

- CW laser strategies for multi-parameter measurements of high-speed flows containing NO

Schematic for NO LIF experiments

# 5. Working examples - 1

- CW laser strategies for multi-parameter measurements of high-speed flows containing NO

# 5. Working examples - 2

- TDL mass flux sensor
  - Full-scale aero-engine inlet

Mass Flux = (Air Density) × (Inlet Velocity)

- Air density ρ from measured absorbance of $O_2$
- Measure integrated absorbance on selected oxygen transition with $S(T) \propto 1/T$ :

$$A = S(T) \cdot P_{O_2} \cdot L = \rho_{O_2} \cdot S(T) \cdot (RT) \cdot L$$

$$A \propto \rho_{O2} \propto \rho_{air}$$

- Velocity u from Doppler shift:

$$\Delta\nu = \nu_0 (2\sin\theta)\frac{u}{c}$$

# 5. Working examples - 2

- TDL mass flux sensor
  - Sensor tests in Pratt and Whitney engine inlet

- Bellmouth installed on inlet of commercial engine (Airbus 318)
- Sensor hardware remotely operated in control room
- TDL beams mounted in engine bellmouth

# 5. Working examples - 2

- TDL mass flux sensor
  - P & W mass flux versus TDL sensor measurements

- TDL data agrees well (1.2% in V and 1.5% in ρ) w/ test stand instrumentation
- Flow model employed to account for non-uniformities
- Success in non-uniform flow suggest other potential applications

# Next: Electronic Spectra of Diatomics

- Term Symbols, Molecular Models
- Rigid Rotor, Symmetric Top
- Hund's Cases
- Quantitative Absorption