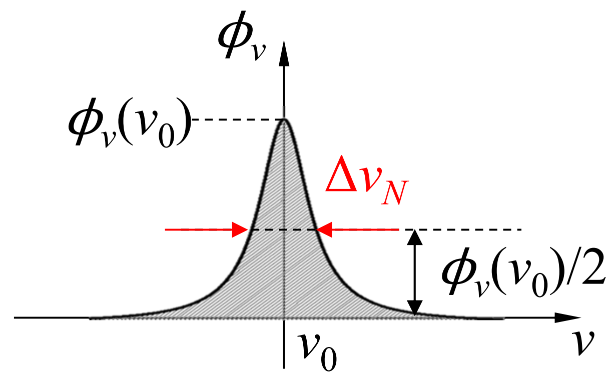
Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 6: Spectral Lineshapes

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

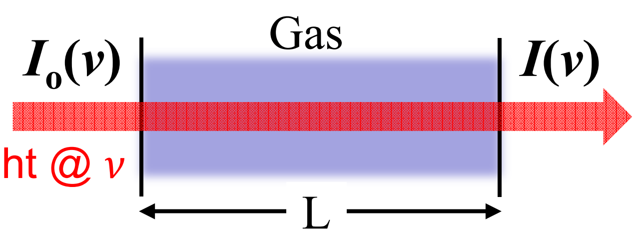


A typical lineshape function

1. Background introduction

- Beer's Law

Recall:



Collimated light @ ν

absorption coefficient @ ν, cm^{-1}

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

intensity or power @ ν spectral intensity @ ν

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

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

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

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

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

← The lineshape function

1. Background introduction

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

$$S_{12},\mathrm{cm}^{-2} = \left(S_{12},\mathrm{cm}^{-1}\mathrm{s}^{-1}\right)/c \qquad \boxed{k_\nu,\mathrm{cm}^{-1} = S_{12}\left[\mathrm{cm}^{-1}\cdot\mathrm{s}^{-1}\right]\phi[\mathrm{s}]}$$

    - Another common form

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

Partial pressure of absorber

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

    - $\left(S_{12},\mathrm{cm}^{-2}\mathrm{atm}^{-1}\right)\left(P_i,\mathrm{atm}\right)$

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

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

✎Notes:

1. $\frac{n_1}{P_i,\mathrm{atm}}$

$$= \frac{n_1}{n_i kT/1.013\times10^6\,\mathrm{dynes/cm^2atm}}$$

$$= \frac{1}{kT}\underline{\left(\frac{n_1}{n_i}\right)}10^6$$

← Boltzmann fraction

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

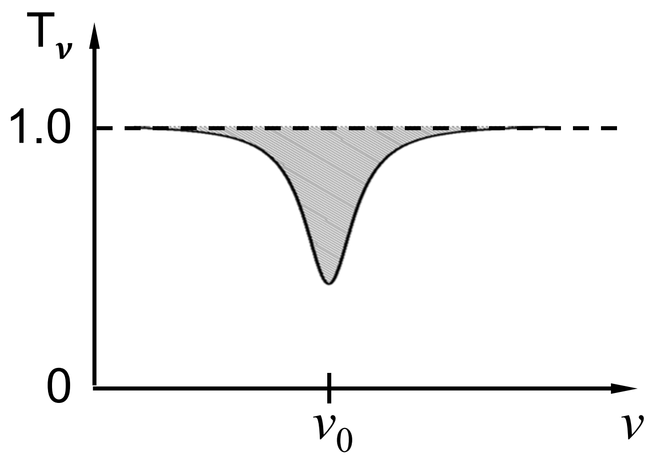
$$P_i,\mathrm{atm} = (P,\mathrm{atm})\underline{(\chi_i)}$$

← Mole fraction

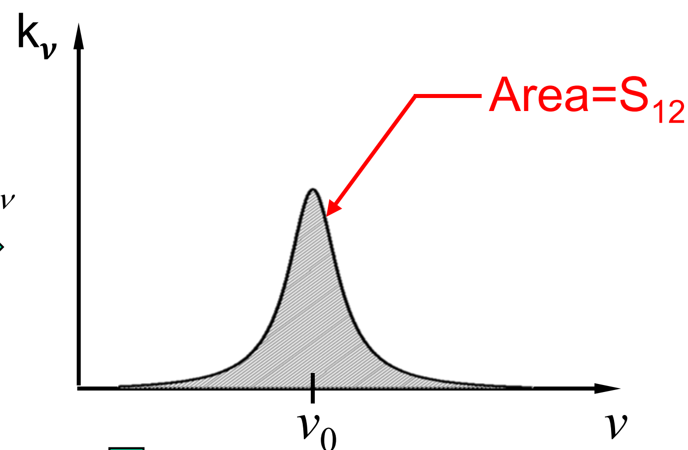
1. Background introduction

- How are S_{12} and ϕ measured?

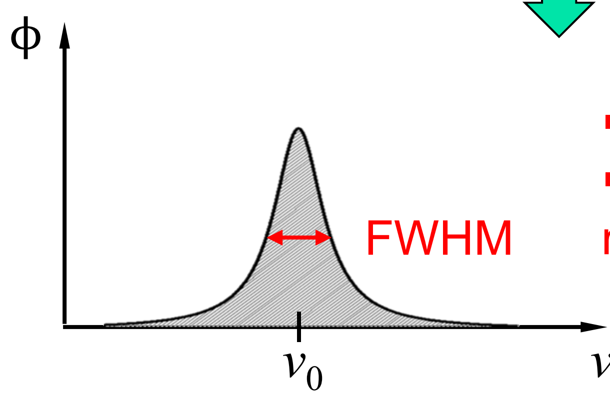
➡ High-resolution absorption experiments



$$-\ln\left(I/I_0\right)_\nu$$



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



- Area=1
- Shape determined by main broadening mechanism

2. Types of line broadening

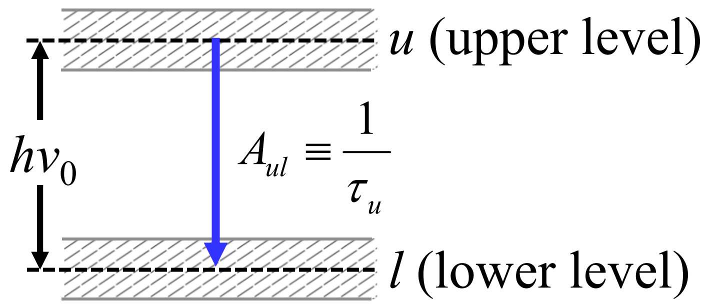
- Brief overview

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

2. Types of line broadening

- Natural line broadening

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



Decay rate

ΔE_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:

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

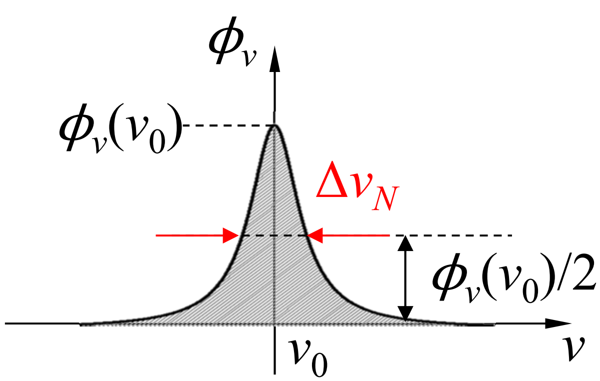
$$\Delta\omega_N, \mathrm{cm}^{-1} = \Delta\nu_N / c = 5\times 10^{-4}\,\mathrm{cm}^{-1}$$

   - Vib-rot transitions

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

   - 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)

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

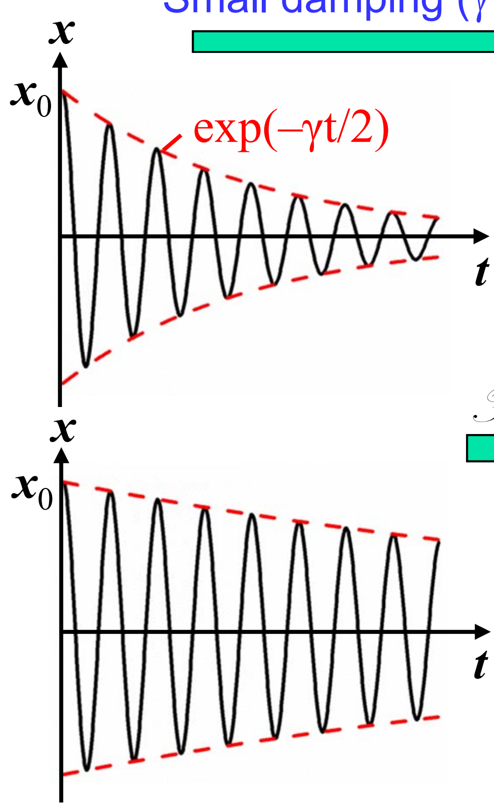
$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = 0,\ \ \omega_0^2 = k/m$$
$$x(0) = x_0, \dot{x}(0) = 0$$

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

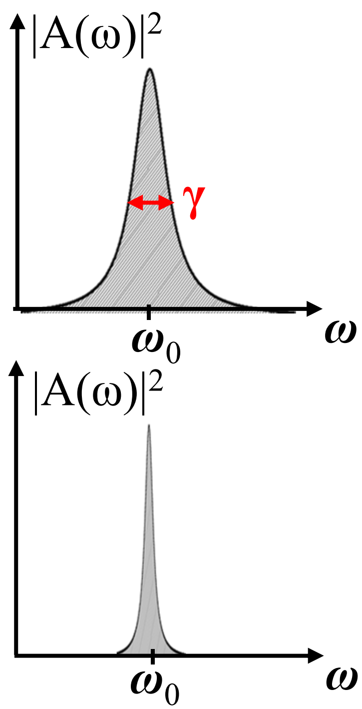
Small damping ($\gamma \ll \omega_0$)

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

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



$\mathscr{F}$



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

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

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

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

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

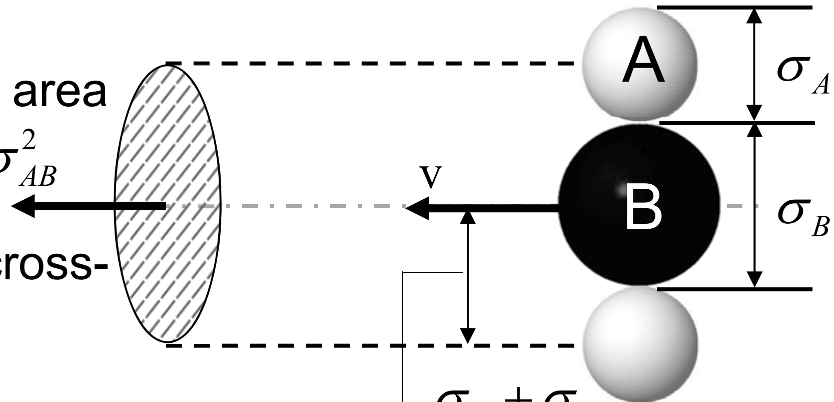
2. Types of line broadening

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

Effective area

$A = \pi\sigma_{AB}^2$

Optical cross-section



σ_A

σ_B = optical collision diameter of B

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

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

#/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

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

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

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

$2\gamma_A$ = colli. 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 $\underset{\mathrm{cm}^{-1}/\mathrm{atm}}{2\gamma(T)} = \underbrace{2\gamma^{300}}_{\approx 0.1\mathrm{cm}^{-1}/\mathrm{atm}}(300/T)^n \leftarrow$ n=1/2 for hard sphere

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 cm^{-1}/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) cm^{-1}/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

$$\Delta\nu_C = P\Big(X_{N_2}\cdot 2\gamma_{CO-N_2} + X_{H_2O}\cdot 2\gamma_{H_2O-N_2} + X_{CO}\cdot 2\gamma_{CO-CO} + X_{CO_2}\cdot 2\gamma_{CO-CO_2} + X_{O_2}\cdot 2\gamma_{CO-O_2}\Big)$$

$$= 0.115\mathrm{cm}^{-1}$$

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

Species00	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)

$$\left|\nu_{app} - \nu_{act}\right| = \nu_{act} u / c = u / \lambda \Rightarrow \nu_{app} = \nu_{act}\left(1 - \underbrace{u}_{\text{molec. velocity along beam path}} / c\right)$$

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

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

$$\boxed{\begin{aligned} \Delta\nu_D(\mathrm{FWHM}) &= 2\sqrt{\frac{2kT\ln 2}{mc^2}}\,\nu_0 \\ \Delta\nu_D(\mathrm{FWHM}) &= 7.17\times 10^{-7}\,\nu_0\sqrt{\frac{T}{M}} \end{aligned}}$$

g/mole of emitter/absorber

- Aside:

Maxwellian velocity distribution

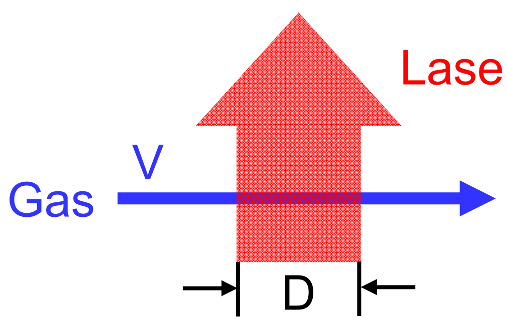
$$f(U_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mU_x^2}{2kT}\right)$$

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)
  - Transit-time broadening

- Another type of lifetime-limited broadening is transit-time broadening



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
  (λ=600nm, $\nu=5\mathrm{x}10^{14}\mathrm{s}^{-1}$)

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

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

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

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

- Vib-rot transition
  (λ=6μm, $\nu=5\mathrm{x}10^{13}\mathrm{s}^{-1}$)

$\rightarrow \lambda_{IR}=10\lambda_{vis}$

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

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

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

2nd Example:

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

- Electronic transition
  (λ=600nm, $\nu=5\mathrm{x}10^{14}\mathrm{s}^{-1}$)

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

- Vib-rot transition
  (λ=6μm, $\nu=5\mathrm{x}10^{13}\mathrm{s}^{-1}$)

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

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

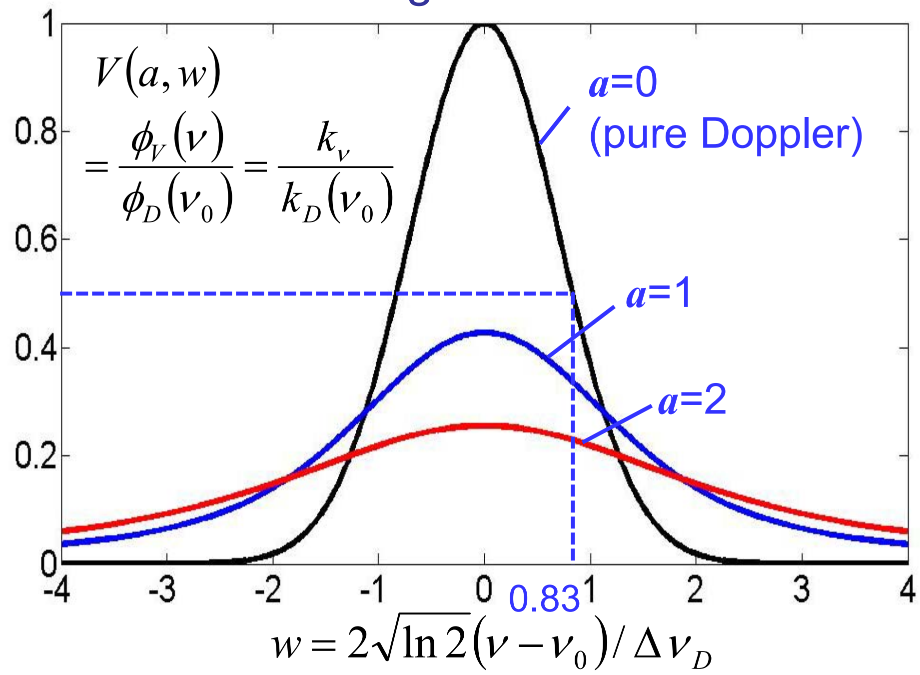
  - Many conditions require consideration of both effects

    Together ➡ Voigt profile!

3. Voigt Profiles

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

Voigt function



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 (X_A) — coll. width/atm for A as coll. partner ($2\gamma_A$), $\propto \sqrt{1/T}$

  - 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 σ_{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

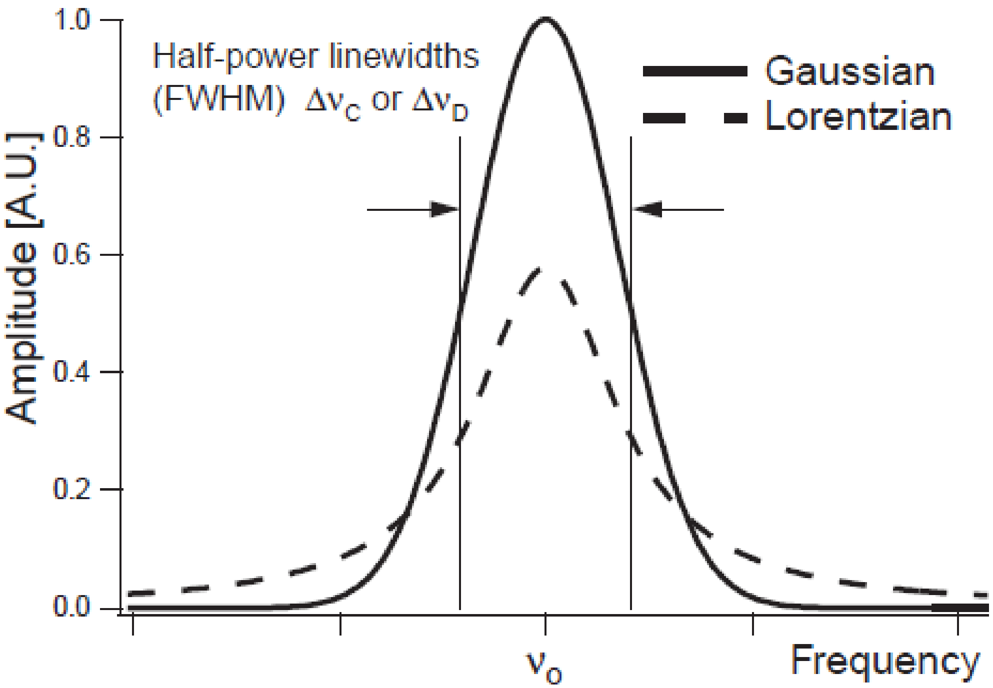
- Doppler broadening review
  - $$\phi(\nu)=\underbrace{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D}}_{\phi(\nu_0)}\exp\left[-\left(\frac{2\sqrt{\ln 2}}{\Delta\nu_D}(\nu-\nu_0)\right)^2\right]$$ Gaussian form
  - $$\underbrace{\Delta\nu_D}_{\text{FWHM}},\mathrm{s}^{-1}=2\left(\frac{2kT\ln 2}{mc^2}\right)^{1/2}\nu_0=7.17\times10^{-7}\nu_0\sqrt{T/\underbrace{M}_{\t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

$$\Delta\nu_D(\lambda=600\mathrm{nm},M=30)=0.35\times10^{10}\mathrm{s}^{-1}(3000\mathrm{K})\approx0.12\mathrm{cm}^{-1}$$
$$=0.1\times10^{10}\mathrm{s}^{-1}(300\mathrm{K})\approx0.03\mathrm{cm}^{-1}$$

  - 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 ϕ_D and ϕ_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

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

the "Voigt function" (V≤1)

✐Notes:

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

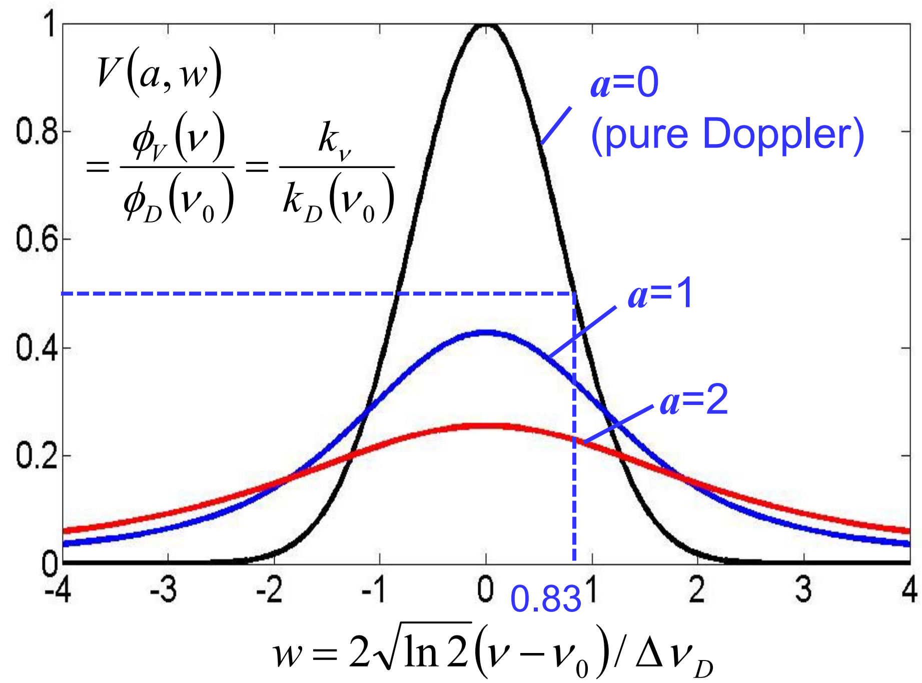
Spec. abs. coeff. — k_ν

k_0 — $k_D(\nu_0)$, the line-center spec. abs. coeff. for Doppler broadening

Recall: $k_\nu = S\phi$

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

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



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

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

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, ν_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 ν) 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, ν_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 ν) 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

    ➡ differences in the energy level spacings

    ➡ pressure shift

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

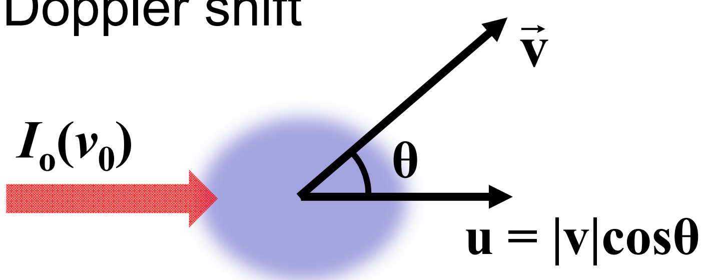
δ_A: cm^{-1}/atm

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

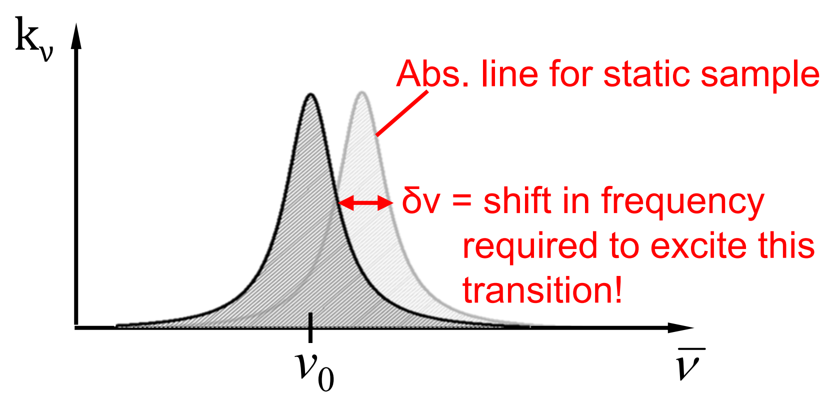
✐Notes:

1. While $2\gamma>0$, 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: $0.1<\alpha<2.3$
➡ 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

What is P_{Na}?

λ = 589nm, T = 1600K, P = 1atm

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

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

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

$$\left(589 \times 10^{-7}\,\text{cm}\right)^{-1} = 16978\text{cm}^{-1}$$

$$\Delta\nu_D = \left(7.17 \times 10^{-7}\right)\left(16978\text{cm}^{-1}\right)\left(\frac{1600}{23}\right)^{1/2}$$

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

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

Interpolate Voigt table

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

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

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

$$= 9.39 \times 0.2852 = 2.68\text{cm}$$

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

Could also have solved for T from lineshape data

4. Uses of quantitative lineshape measurements

- Examples
  - 2^{nd} Example: Atomic H velocity

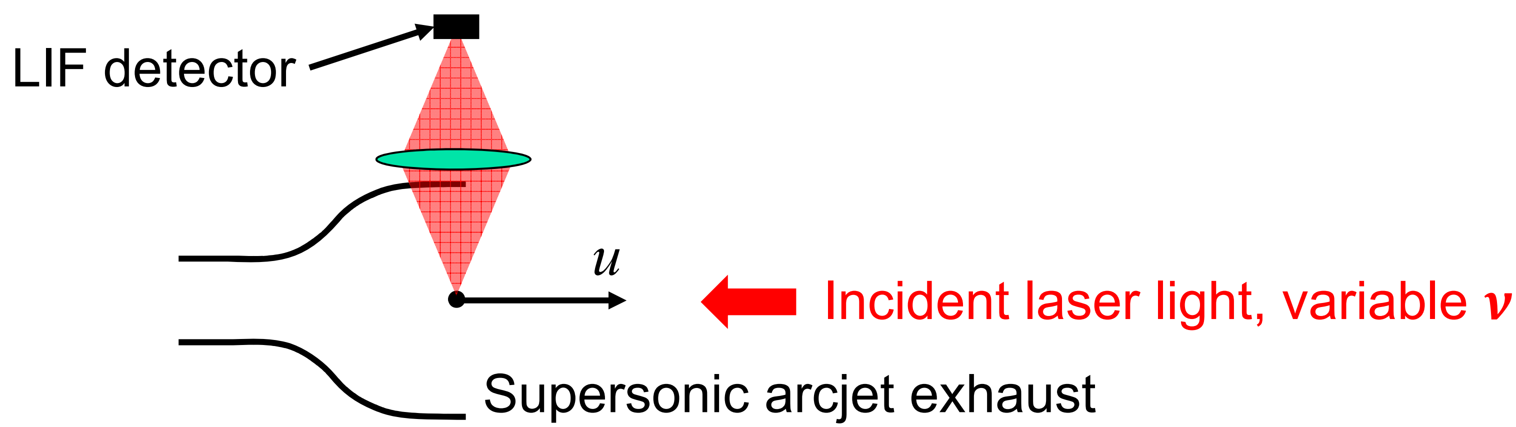
LIF (Laser Induced Fluorescence) in an arcjet thruster is used to measure the Doppler shift of atomic hydrogen at 656nm.

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

Use line position to infer velocity

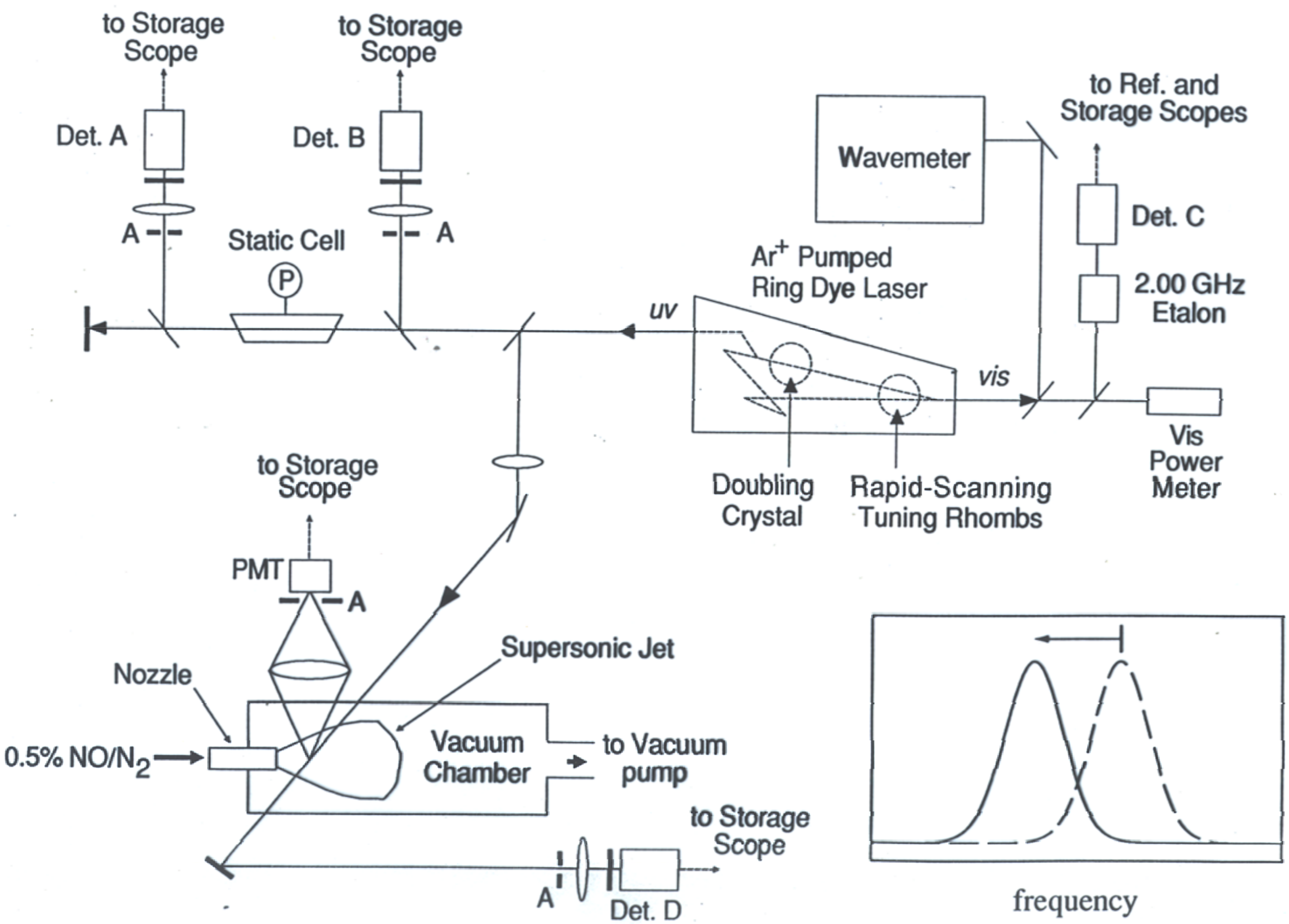
The corresponding velocity component is found

$$u = \frac{c\delta\nu}{\nu_0} = \frac{3\times10^8\text{m/s}\times0.70\text{cm}^{-1}}{15.232\text{cm}^{-1}} = 13800\text{m/s}$$



5. Working examples - 1

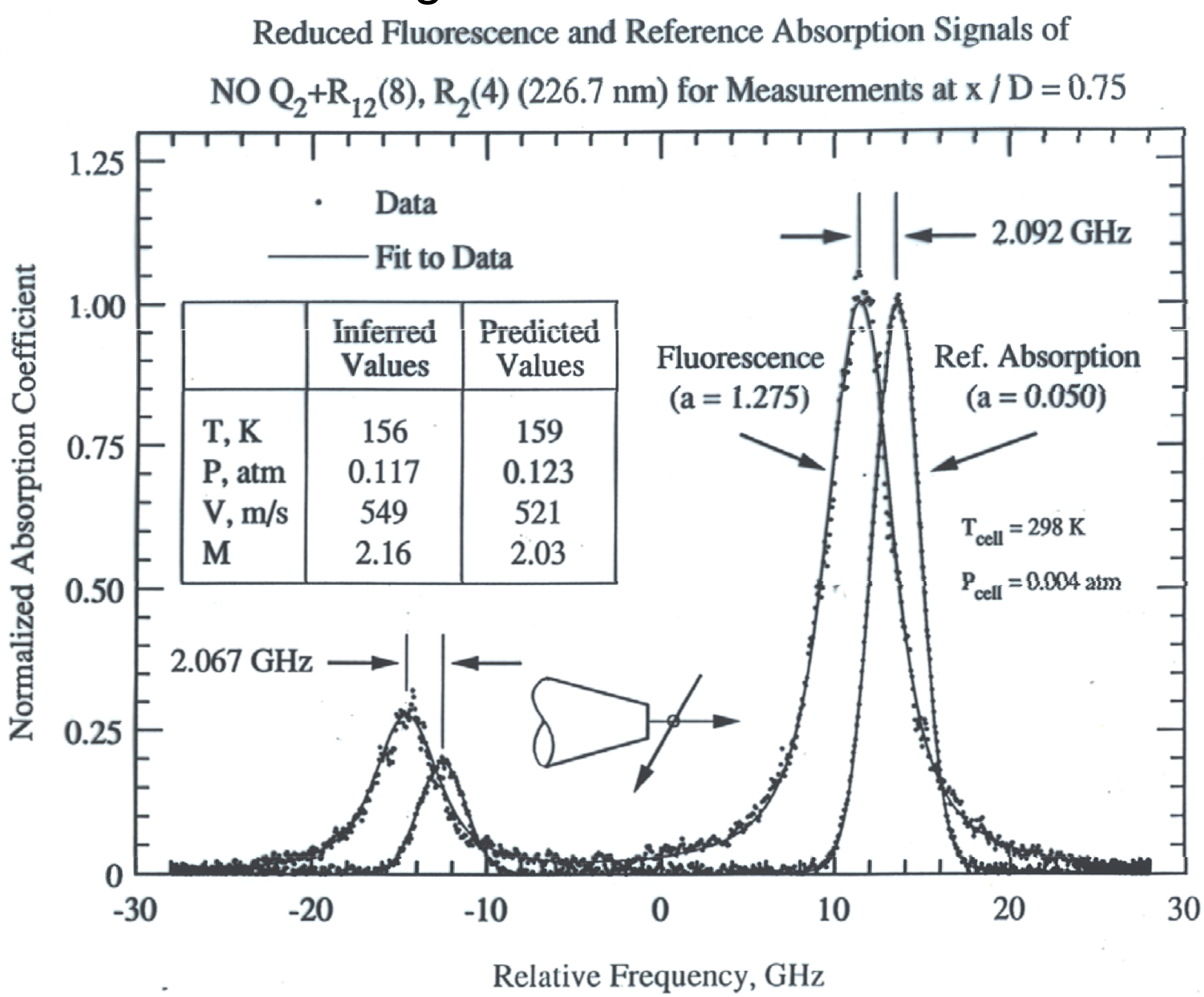
- CW laser strategies for multi-parameter measurements of high-speed flows containing NO



Schematic for NO LIF experiments

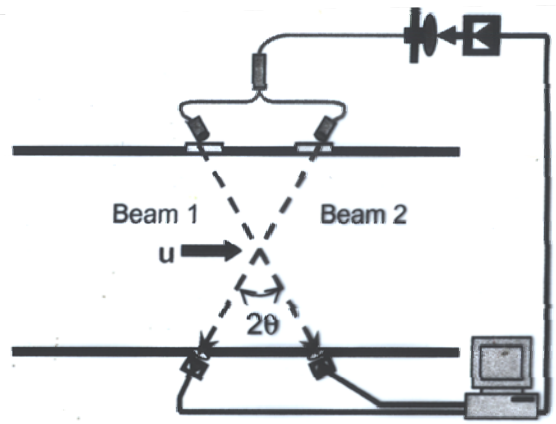
5. Working examples - 1

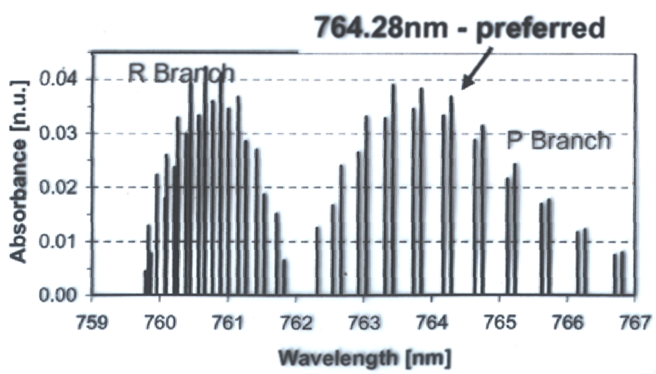
- CW laser strategies for multi-parameter measurements of high-speed flows containing NO



5. Working examples - 2

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



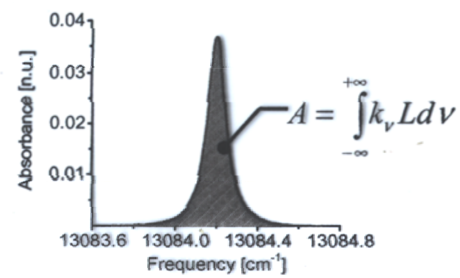


Mass Flux = (Air Density) × (Inlet Velocity)

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

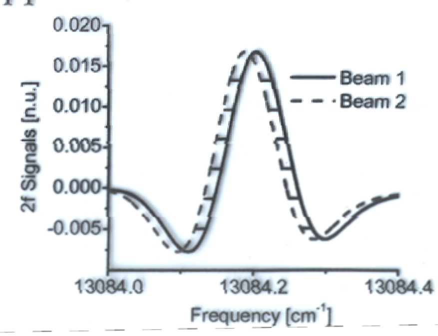
$$A = S(T)\cdot P_{O_2}\cdot L = \rho_{O_2}\cdot S(T)\cdot (RT)\cdot L$$

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



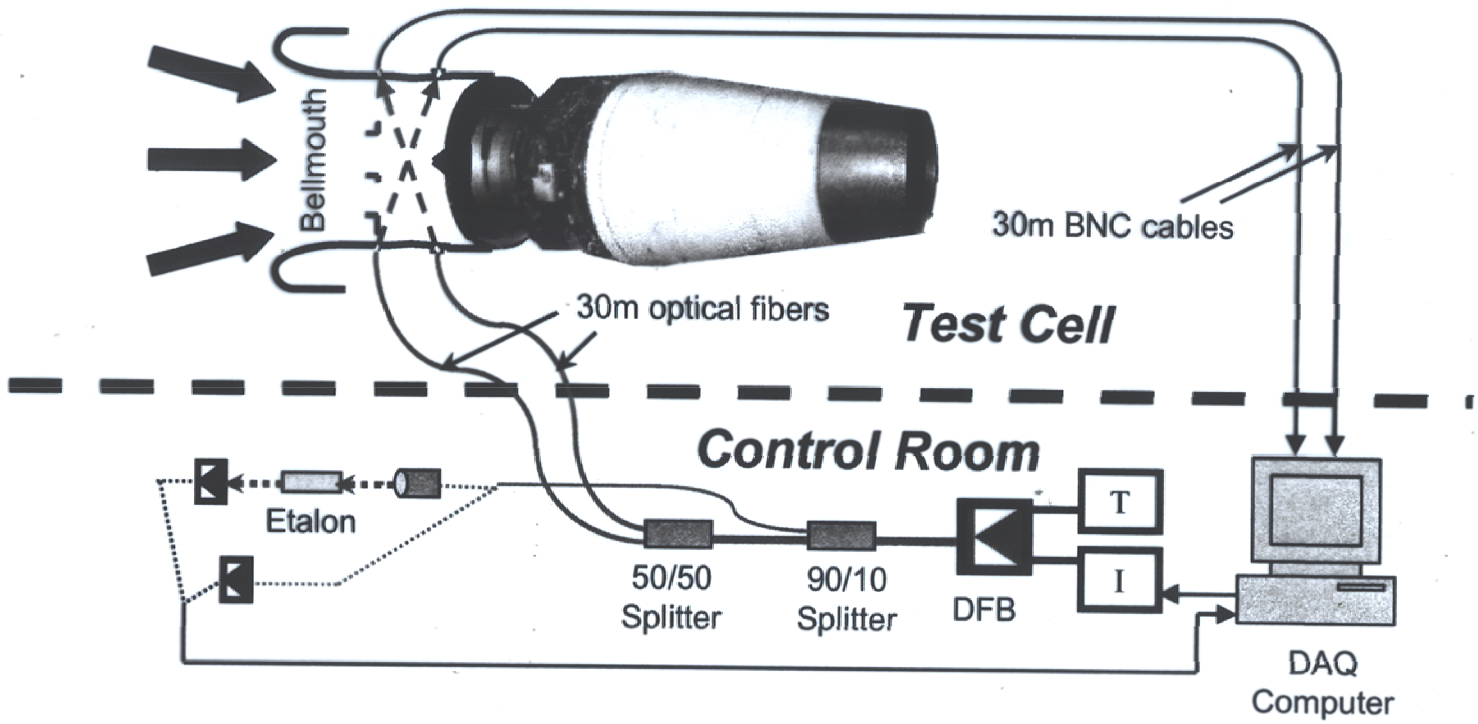
- Velocity u from Doppler shift:

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



5. Working examples - 2

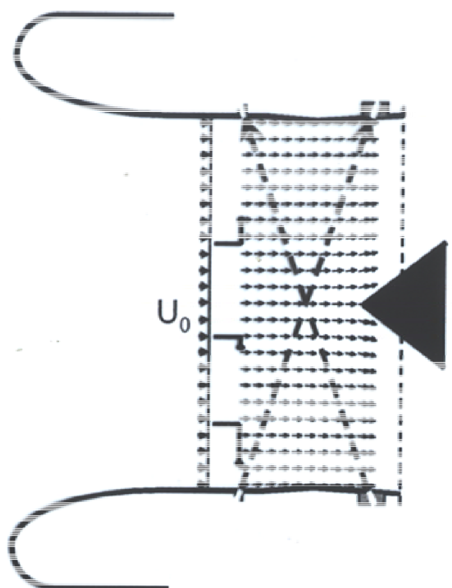
- TDL mass flux sensor
  - Sensor tests in Pratt and Whitney engine inlet

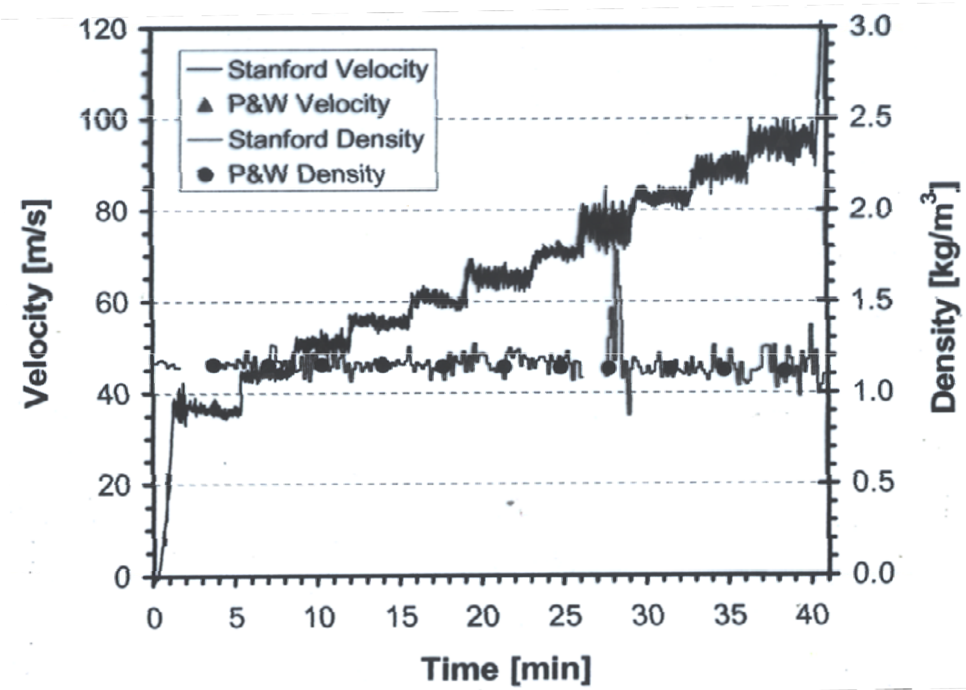


- Bellmouth installed on inlet of commercial engine (Airbus 318)
- Sensor hardware remotely operated in control room
- TDL beams mounted in engine bellmouth

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