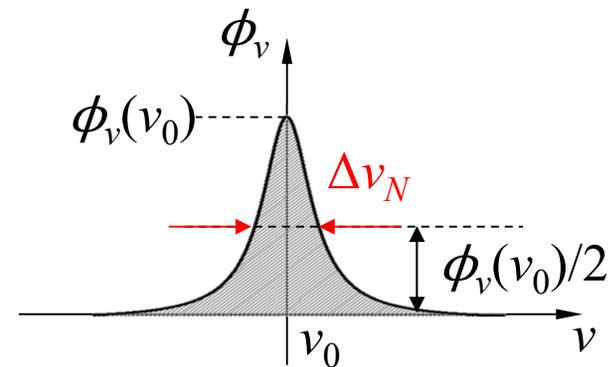


Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 6: Spectral Lineshapes

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

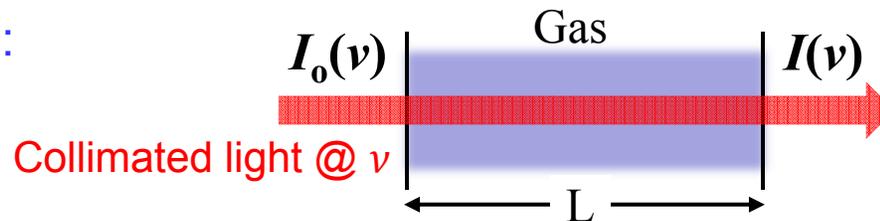


A typical lineshape function

1. Background introduction

- Beer's Law

Recall:



absorption coefficient @ 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

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

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

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

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

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

← The lineshape function

1. Background introduction

- Alternate forms of ν , ϕ , S_{12}

- ν $\nu, s^{-1} = \frac{c}{\lambda} = c(\bar{\nu}, cm^{-1})$

- ϕ $\phi, cm = c(\phi, s)$

- S_{12} ■ A common form of S

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

- Another common form

$$S_{12}, cm^{-2} / atm = (S_{12}, cm^{-2}) / (P_i, atm) = \frac{S_{12}, cm^{-2}s^{-1}}{cP_i, atm} \quad \text{Partial pressure of absorber}$$

 Notes:

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

$$= \frac{n_1}{n_i kT / 1.013 \times 10^6 \text{ dynes/cm}^2 \text{ atm}}$$

$$= \frac{1}{kT} \left(\frac{n_1}{n_i} \right) 10^6 \quad \leftarrow \text{Boltzmann fraction}$$

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

$$P_i, atm = (P, atm)(\chi_i) \quad \leftarrow \text{Mole fraction}$$

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

- $(S_{12}, cm^{-2} atm^{-1})(P_i, atm)$

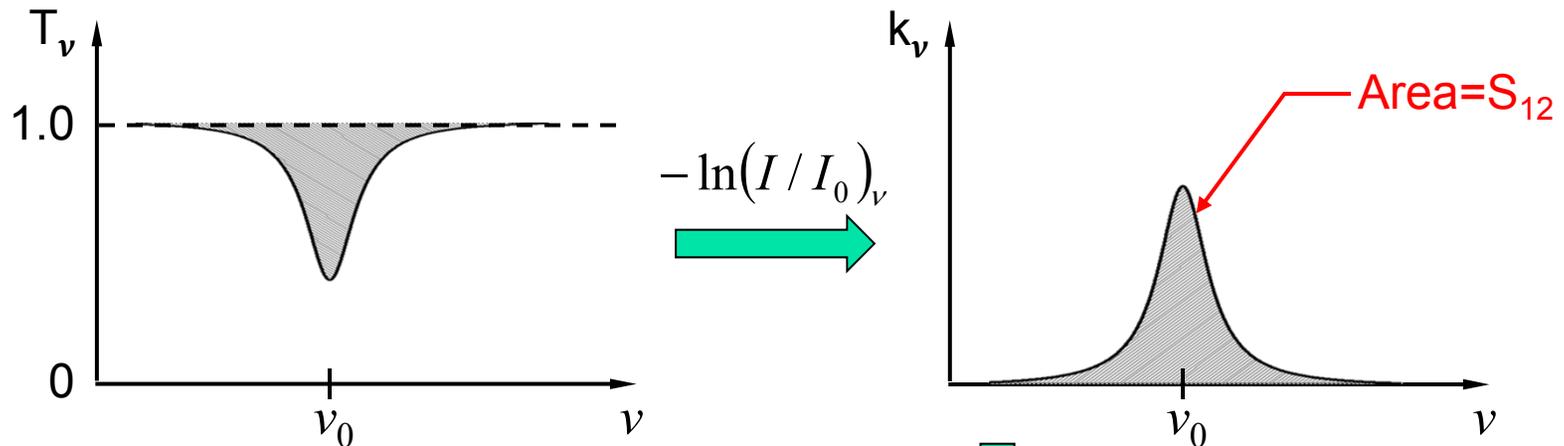
$$= \left(S^*, \frac{cm^{-1}}{molec/cm^2} \right) \left(n_i, \frac{molec}{cm^3} \right)$$

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

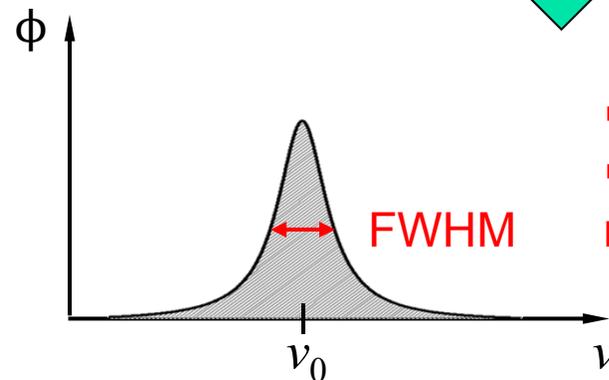
1. Background introduction

- How are S_{12} and ϕ measured?

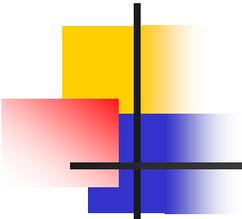
➔ High-resolution absorption experiments



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



- Area=1
- Shape determined by main broadening mechanism



2. Types of line broadening

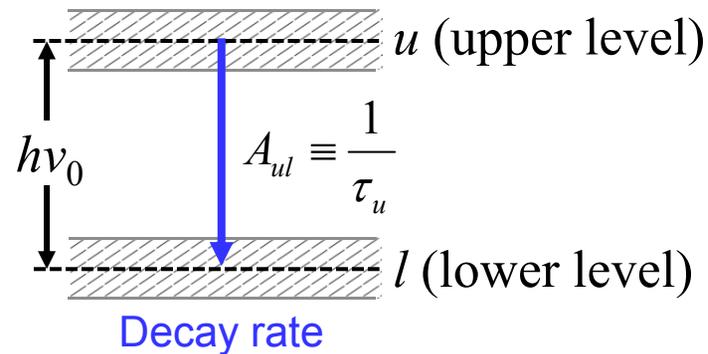
- Brief overview

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

2. Types of line broadening

- Natural line broadening

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



ΔE_u = uncertainty in energy of u

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

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

2. In general

$$\Delta\nu_N = \Delta\nu_u + \Delta\nu_l = \frac{1}{2\pi} \left(\frac{1}{\tau_u} + \frac{1}{\tau_l} \right) \begin{matrix} 0 \text{ for ground state} \\ \text{(natural broadening)} \end{matrix}$$

2. Types of line broadening

- Natural line broadening

3. Typical values

- Electronic transitions:

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

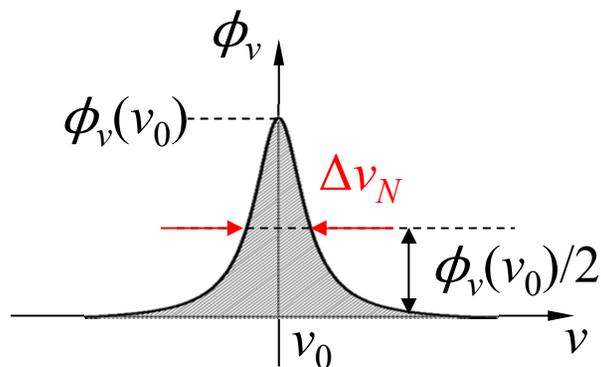
$$\Delta \omega_N, \text{ cm}^{-1} = \Delta \nu_N / c = 5 \times 10^{-4} \text{ cm}^{-1}$$

- Vib-rot transitions

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

- 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) $\phi_{\text{max}} = \phi(\nu_0) = \frac{2}{\pi} \frac{1}{\Delta \nu_N}$
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
 $\gamma = \Delta v_n \sim 1/\Delta\tau \cdot 2\pi$
 in units of s^{-1}

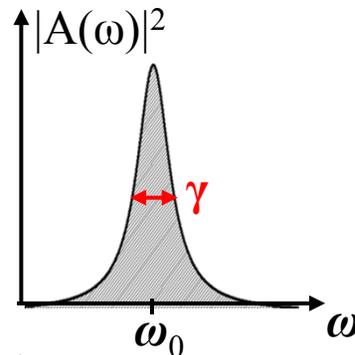
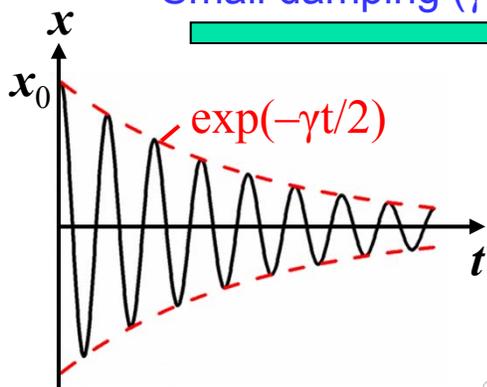
$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = 0, \quad \omega_0^2 = k/m \quad \rightarrow \quad x(t) = x_0 \exp(-\gamma t/2) [\cos \omega t + (\gamma/2\omega) \sin \omega t]$$

$$x(0) = x_0, \quad \dot{x}(0) = 0 \quad \rightarrow \quad \omega = (\omega_0^2 - \gamma^2/4)^{1/2}$$

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

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

Amplitude of $x(t)$ decrease \rightarrow
 frequency of emitted radiation
 is no longer monochromatic



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

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

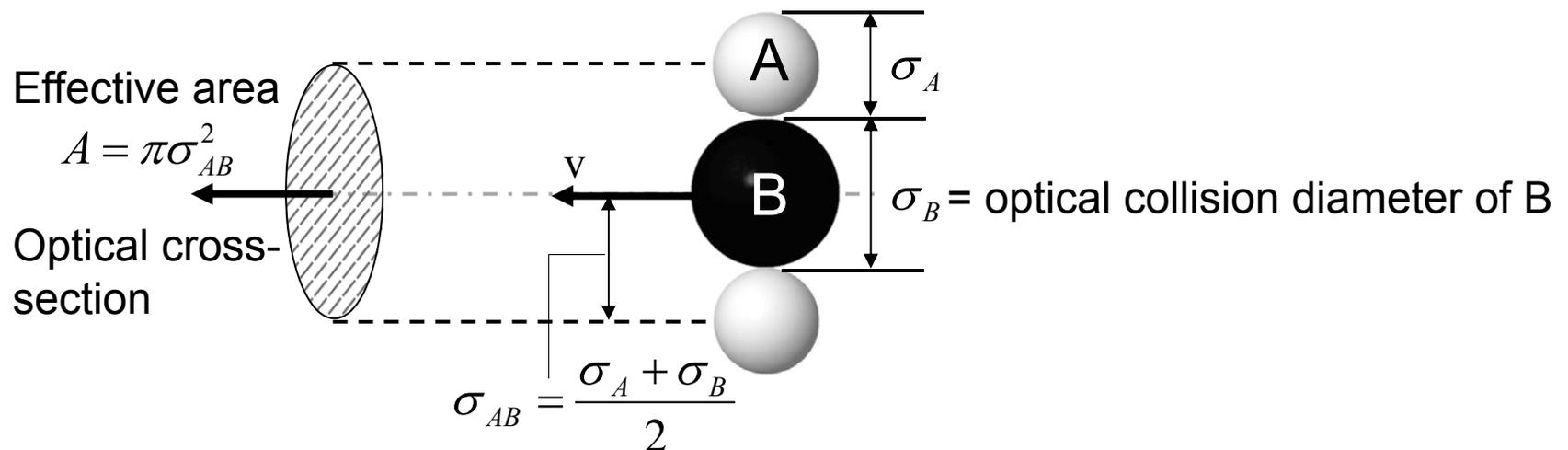
$$= \frac{x_0}{\sqrt{8\pi}} \left(\frac{1}{i(\omega - \omega_0) + \gamma/2} + \frac{1}{i(\omega + \omega_0) + \gamma/2} \right)$$

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

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

2. Types of line broadening

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



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

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

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

For a mixture,

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

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

$P, \text{ dynes/cm}^2 = 1.013 \times 10^6 (P, \text{ atm})$

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

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

$$= (P, \text{atm}) \sum_A X_A \cdot \underbrace{\sigma_{AB}^2 \cdot \sqrt{\frac{8}{\pi \mu_{AB} kT}} \cdot 1.013 \times 10^6}_{2\gamma_A, \text{s}^{-1}/\text{atm}}$$

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

$2\gamma_A = \text{colli. halfwidth, i.e., FWHM per atm. pressure}$

 Notes:

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

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

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

2. Types of line broadening

- Collision broadening

Example: Pressure broadening of CO

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

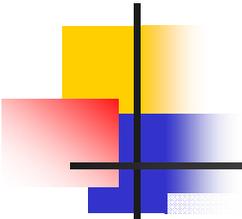
with $2\gamma_A$ in $\text{cm}^{-1}/\text{atm}$

R(9) line of CO's 2nd overtone, 50ppm in Air, 300K, 1.0atm

Species population: 77% N₂, 20% O₂, 2% H₂O (85% humidity) 380ppm CO₂

Species, A	Mole Fraction, X _A	2γ _{CO-A} (300K) cm ⁻¹ /atm
N ₂	0.77	0.116
H ₂ O	0.02	0.232
CO	50e-6	0.128
CO ₂	380e-6	0.146
O ₂	0.21	0.102

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



2. Types of line broadening

- Collision broadening

Some collisional broadening coefficients 2γ [$\text{cm}^{-1}/\text{atm}$] 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 [$\text{cm}^{-1}/\text{atm}$] 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)

$$|v_{app} - v_{act}| = v_{act} u / c = u / \lambda \quad \Rightarrow \quad v_{app} = v_{act} (1 - u / c)$$

↳ molec. velocity along beam path

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

$$\phi(v) = \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta v_D} \exp\left[-\left(\frac{2\sqrt{\ln 2}}{\Delta v_D}(v - v_0)\right)^2\right]$$

$\underbrace{\hspace{10em}}_{\phi(v_0)}$

$$\Delta v_D(\text{FWHM}) = 2\sqrt{\frac{2kT \ln 2}{mc^2}} v_0$$

$$\Delta v_D(\text{FWHM}) = 7.17 \times 10^{-7} v_0 \sqrt{\frac{T}{M}}$$

g/mole of emitter/absorber

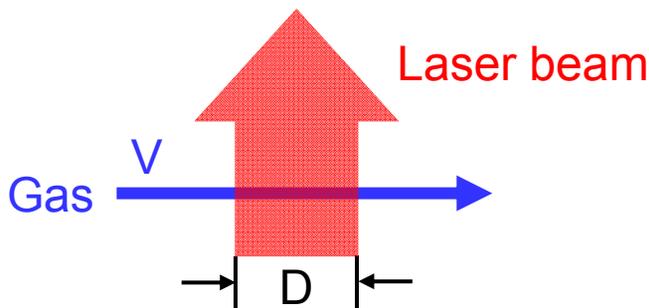
■ Aside:

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



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

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

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
($\lambda=600\text{nm}$, $\nu=5\times 10^{14}\text{s}^{-1}$)

$$\Delta\nu_D = 1.1\times 10^9\text{s}^{-1} \sim 0.04\text{cm}^{-1}$$

$$\Delta\nu_D \gg \Delta\nu_N \sim 10^7\text{s}^{-1}$$

$$\Delta\nu_C \sim 3\times 10^9\text{s}^{-1} = 0.1\text{cm}^{-1}$$

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

- Vib-rot transition
($\lambda=6\mu\text{m}$, $\nu=5\times 10^{13}\text{s}^{-1}$)

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

$$\Delta\nu_D \sim 1.1\times 10^8\text{s}^{-1} \sim 0.004\text{cm}^{-1}$$

$$\Delta\nu_C \sim 3\times 10^9\text{s}^{-1} = 0.1\text{cm}^{-1}$$

$$\therefore \Delta\nu_D \ll \Delta\nu_C$$

2nd Example:

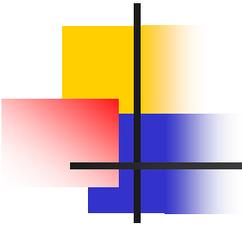
T = 2700K, M = 30g/mole, P = 1atm

- Electronic transition
($\lambda=600\text{nm}$, $\nu=5\times 10^{14}\text{s}^{-1}$)

$$\frac{\Delta\nu_D \sim 0.11\text{cm}^{-1}}{\sim T^{1/2}} > \frac{\Delta\nu_C \sim 0.03\text{cm}^{-1}}{\sim T^{-1/2}}$$

- Vib-rot transition
($\lambda=6\mu\text{m}$, $\nu=5\times 10^{13}\text{s}^{-1}$)

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



2. Types of line broadening

- Conclusions

- Doppler broadening most significant at:

Low P, high T, small λ

- Collision broadening most significant at:

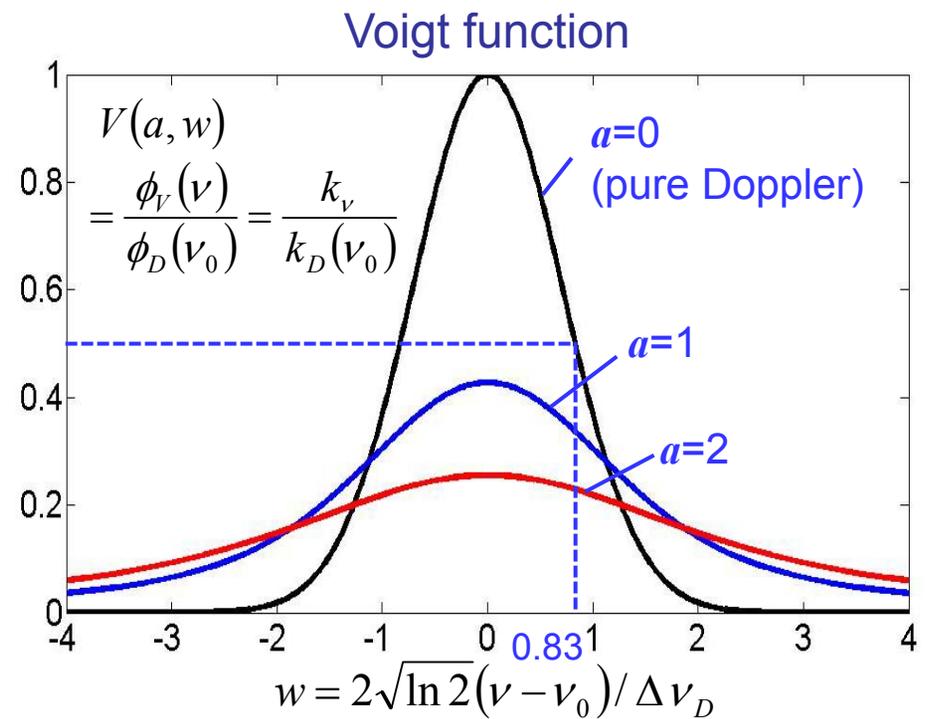
High P, low T, large λ

- 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”

- $$\Delta\nu_C, \text{s}^{-1} = \left(\sum_A X_A \underline{2\gamma_A} \right) (P, \text{atm of mixture})$$

mole fraction of A \uparrow \uparrow coll. width/atm for A as coll. partner, $\propto \sqrt{1/T}$

- Typical value of $2\gamma_A \sim 0.1 \text{cm}^{-1}/\text{atm}$ (or $0.3 \times 10^{10} \text{s}^{-1}/\text{atm}$)

- Aside:
$$2\gamma_A, \text{s}^{-1} = \frac{1}{c} 1.013 \times 10^6 \sigma_{AB}^2 \cdot \sqrt{\frac{8}{\pi \mu_{AB} k T}} \propto \sqrt{\frac{1}{T}}$$

if σ_{AB} is constant

$$0.1 \text{cm}^{-1} / \text{atm} \cdot 3 \times 10^{10} \text{cm/s} = 0.3 \times 10^{10} \text{s}^{-1} / \text{atm}$$

- 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

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

- $$\Delta\nu_D, \text{s}^{-1} = 2\left(\frac{2kT \ln 2}{mc^2}\right)^{1/2} \nu_0 = 7.17 \times 10^{-7} \nu_0 \sqrt{T/M}$$

↑ FWHM ↑ g/mole of absorber/emitter

- Typical value

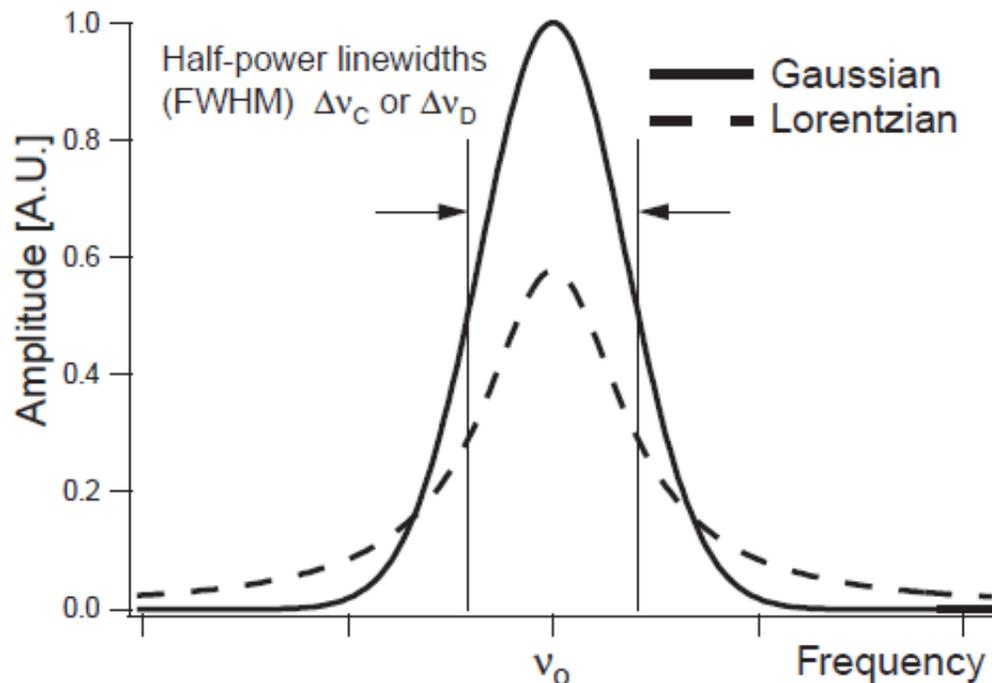
$$\begin{aligned} \Delta\nu_D(\lambda = 600\text{nm}, M = 30) &= 0.35 \times 10^{10} \text{s}^{-1} (3000\text{K}) \approx 0.12 \text{cm}^{-1} \\ &= 0.1 \times 10^{10} \text{s}^{-1} (300\text{K}) \approx 0.03 \text{cm}^{-1} \end{aligned}$$

- 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 $\Delta\nu_C / \Delta\nu_D = 1$

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

- Some exceptions/improved models

- Collision narrowing (low-pressure phenomenon)
 - ➡ Galatry profiles, others, with additional parameters
- Stark broadening ➡ Plasma phenomenon

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

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

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

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

↑
the "Voigt function" ($V \leq 1$)

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

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

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

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" ($V \leq 1$)

Notes:

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

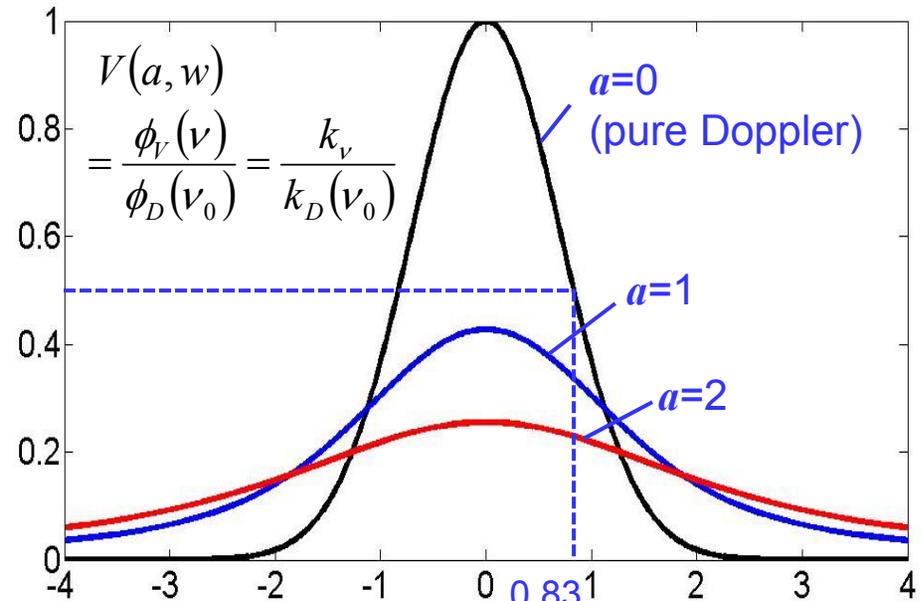
2. $k_\nu = k_0V(a, w)$

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

Recall: $k_\nu = S\phi$

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

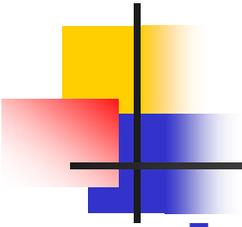
$\therefore \phi_V(\nu_0) = \phi_D(\nu_0) \cdot \exp(a^2)\text{erfc}(a)$



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

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

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



3.2. Voigt profile

- Voigt table

$w \setminus a$	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" ($V \leq 1$)

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
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3.2. Voigt profile

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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

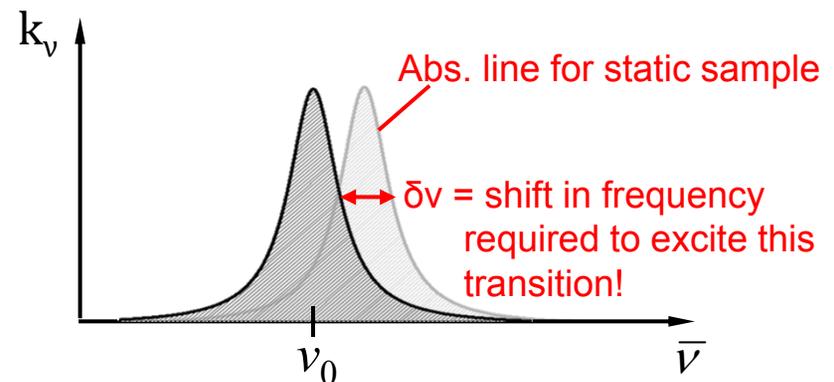
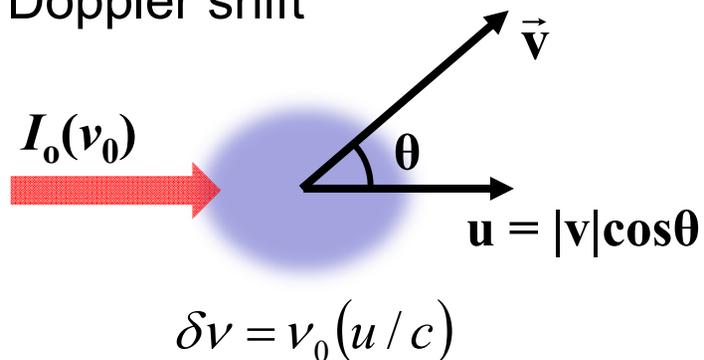
$$\Delta \nu_S = P \sum_A X_A \delta_A \quad \leftarrow \text{cm}^{-1}/\text{atm}$$

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

Notes:

1. While $2\gamma > 0$, δ can be + or -
2. E.g., average values for IR H₂O spectra: $\delta = -0.017 \text{ cm}^{-1}/\text{atm}$, $M=0.96$

- Doppler shift



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 \uparrow Pressure \uparrow Species mole fraction \uparrow 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

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

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

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

Large $\Delta E''$ 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

$$\lambda = 589\text{nm}, T = 1600\text{K}, P = 1\text{atm}$$

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

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

Interpolate Voigt table 

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

$$\phi_D(\nu_0) = \frac{2}{\Delta \nu_D} \sqrt{\frac{\ln 2}{\pi}} = \frac{2}{0.10} \sqrt{\frac{\ln 2}{\pi}} = 9.39\text{cm}^{-1}$$

$$\begin{aligned} \phi(\nu_0) &= \phi_D(\nu_0) V(0) \\ &= 9.39 \times 0.2852 = 2.68\text{cm}^{-1} \end{aligned}$$

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

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

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

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

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

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

Could also have solved for T from lineshape data

4. Uses of quantitative lineshape measurements

- Examples

- 2nd Example: Atomic H velocity

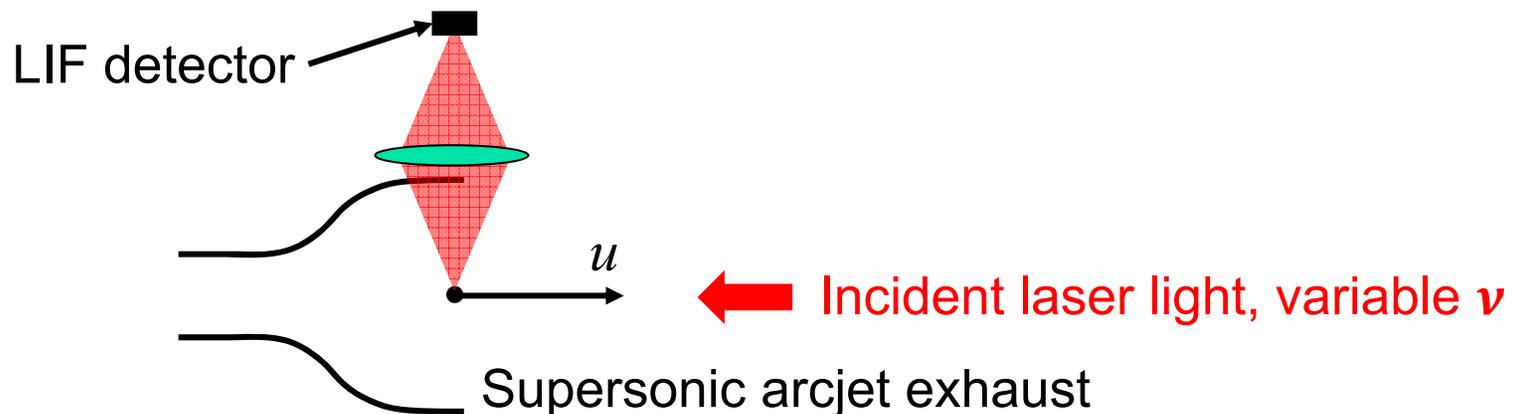
LIF (Laser Induced Fluorescence) in an arcjet thruster is used to measure the Doppler shift of atomic hydrogen at 656nm.

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

Use line position to infer velocity

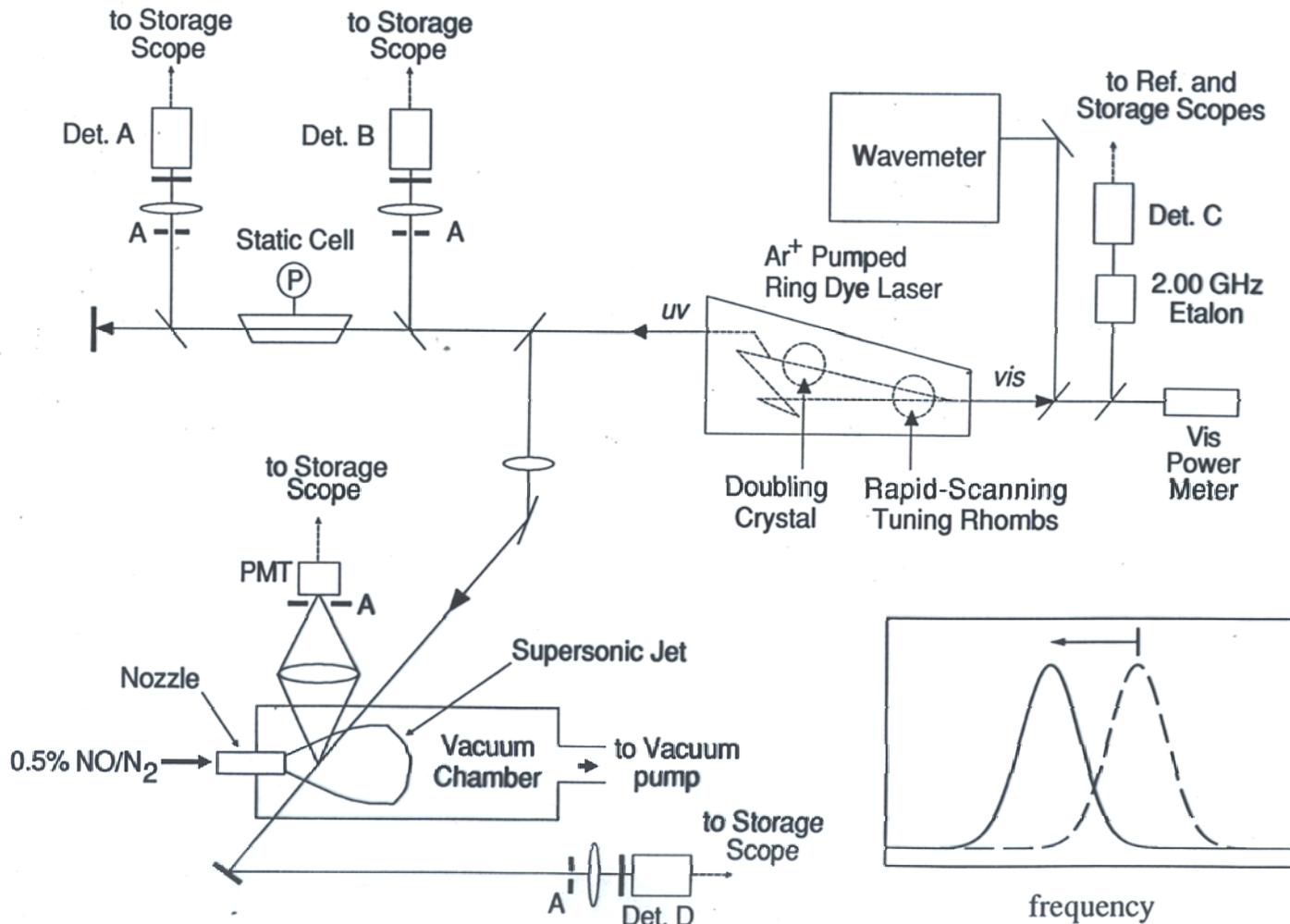
The corresponding velocity component is found

$$u = \frac{c\delta\nu}{\nu_0} = \frac{3 \times 10^8 \text{ m/s} \times 0.70 \text{ cm}^{-1}}{15.232 \text{ cm}^{-1}} = 13800 \text{ m/s}$$

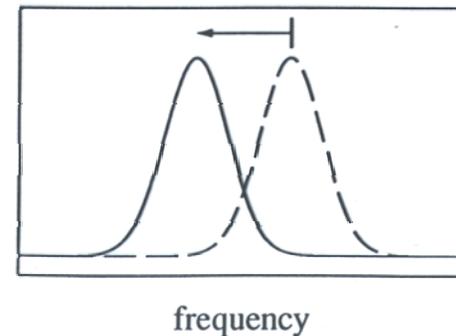


5. Working examples - 1

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



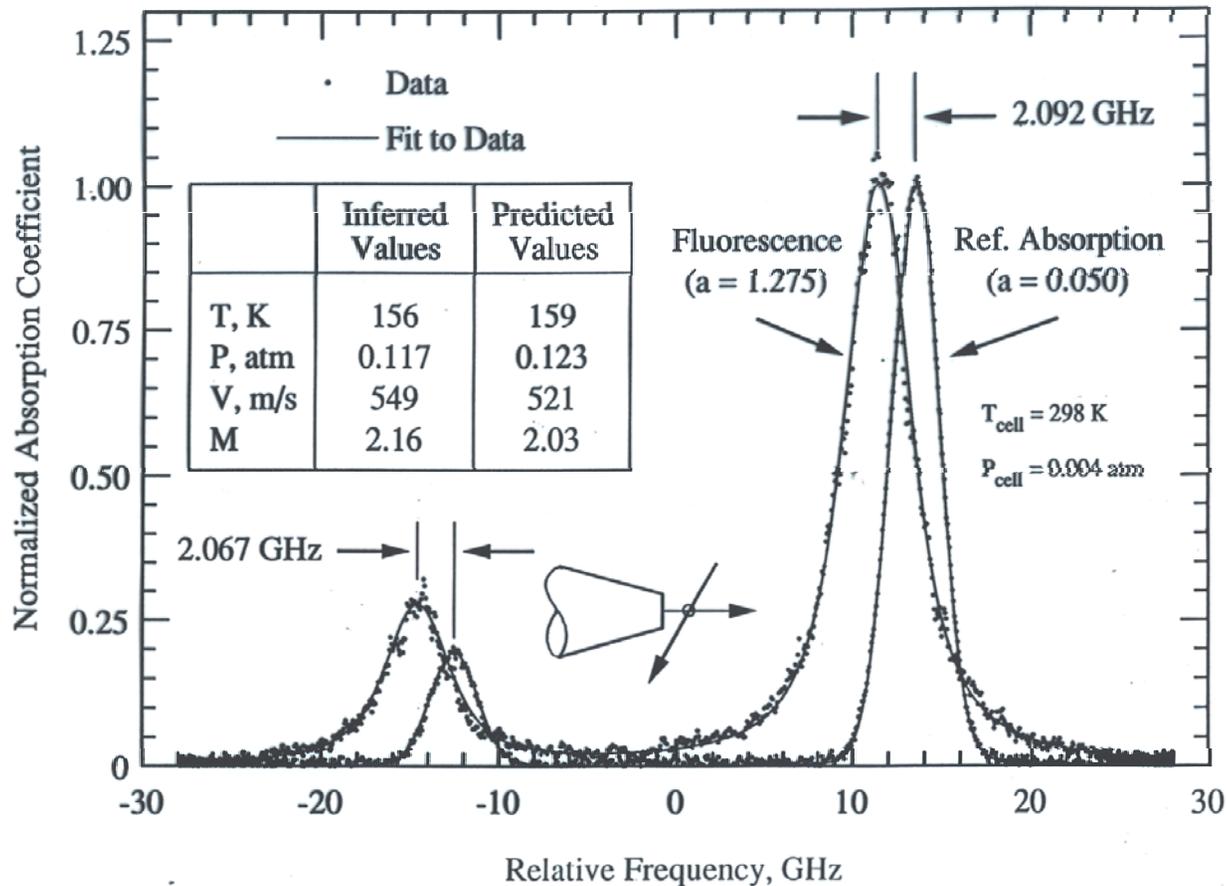
Schematic for NO LIF experiments



5. Working examples - 1

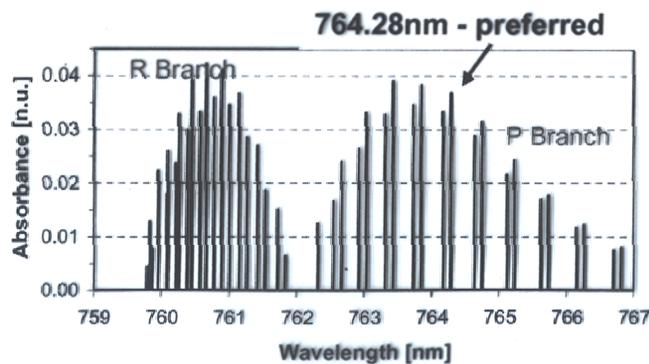
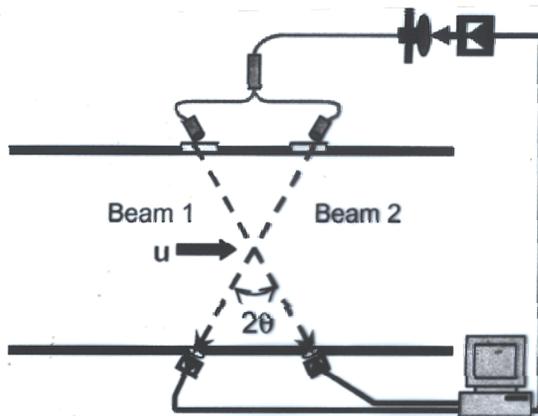
- CW laser strategies for multi-parameter measurements of high-speed flows containing NO

Reduced Fluorescence and Reference Absorption Signals of
 NO $Q_2+R_{12}(8), R_2(4)$ (226.7 nm) for Measurements at $x/D = 0.75$



5. Working examples - 2

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

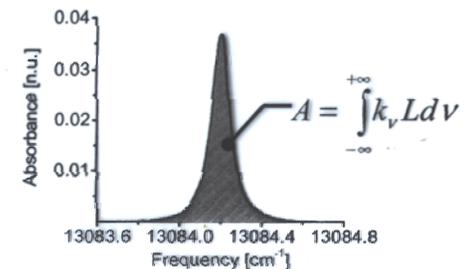


Mass Flux = (Air Density) × (Inlet Velocity)

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

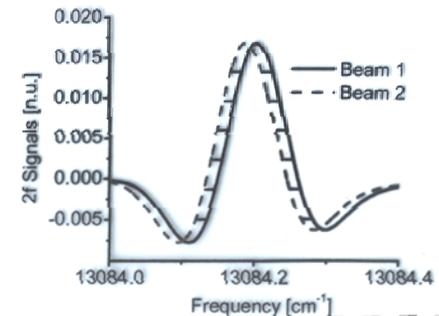
$$A = S(T) \cdot P_{O_2} \cdot L = \rho_{O_2} \cdot S(T) \cdot (RT) \cdot L$$

$$A \propto \rho_{O_2} \propto \rho_{air}$$



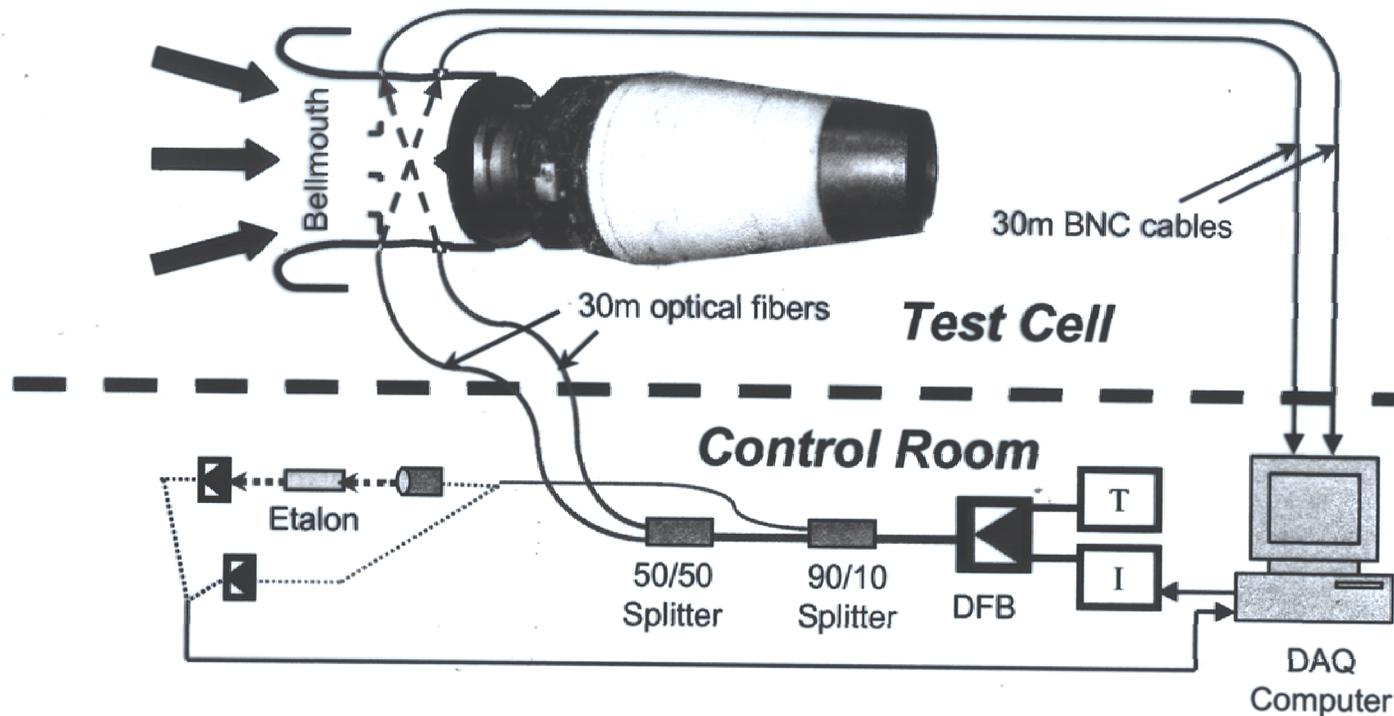
- Velocity u from Doppler shift:

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



5. Working examples - 2

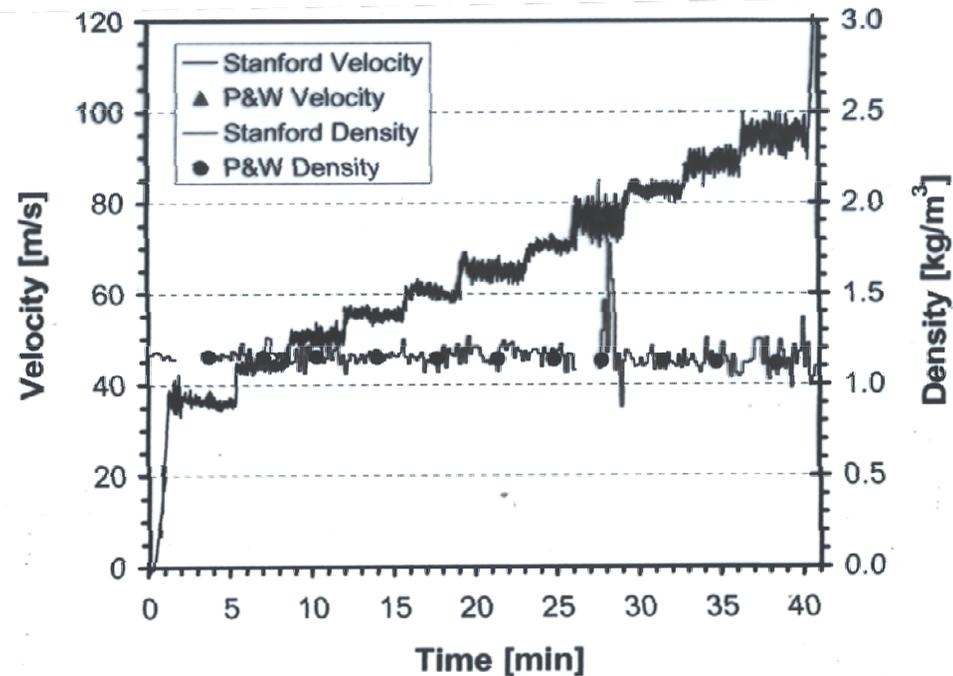
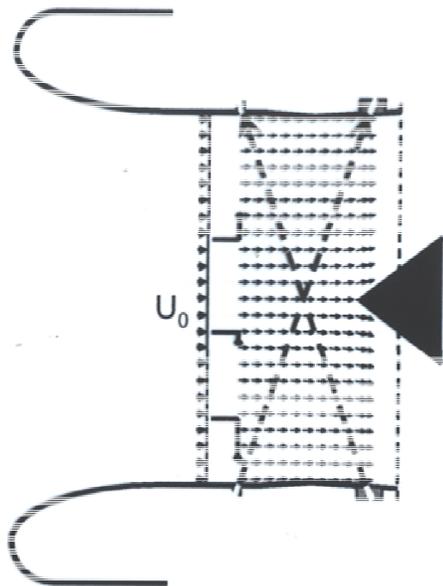
- TDL mass flux sensor
 - Sensor tests in Pratt and Whitney engine inlet



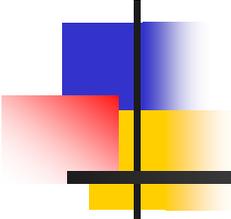
- Bellmouth installed on inlet of commercial engine (Airbus 318)
- Sensor hardware remotely operated in control room
- TDL beams mounted in engine bellmouth

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