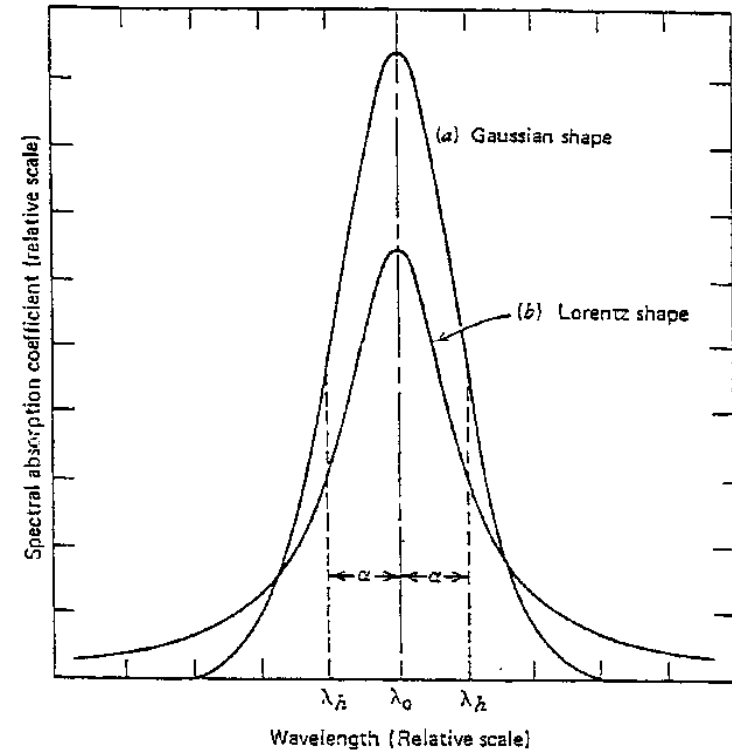
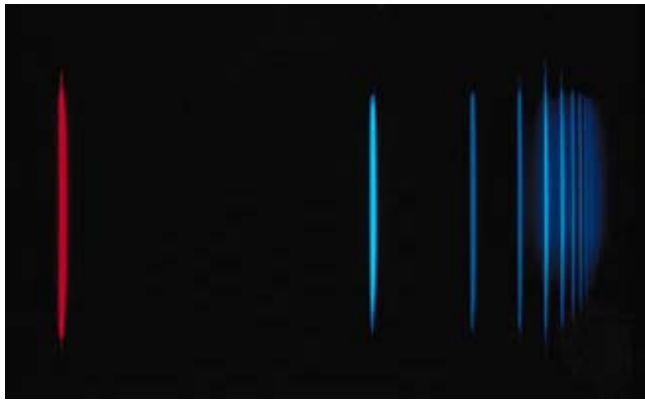


Line shapes



Sept 4 2008

CHEM 5161

What determines the line width ?

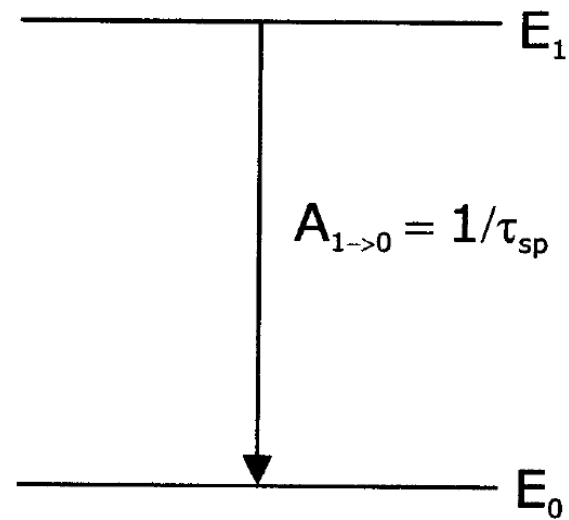
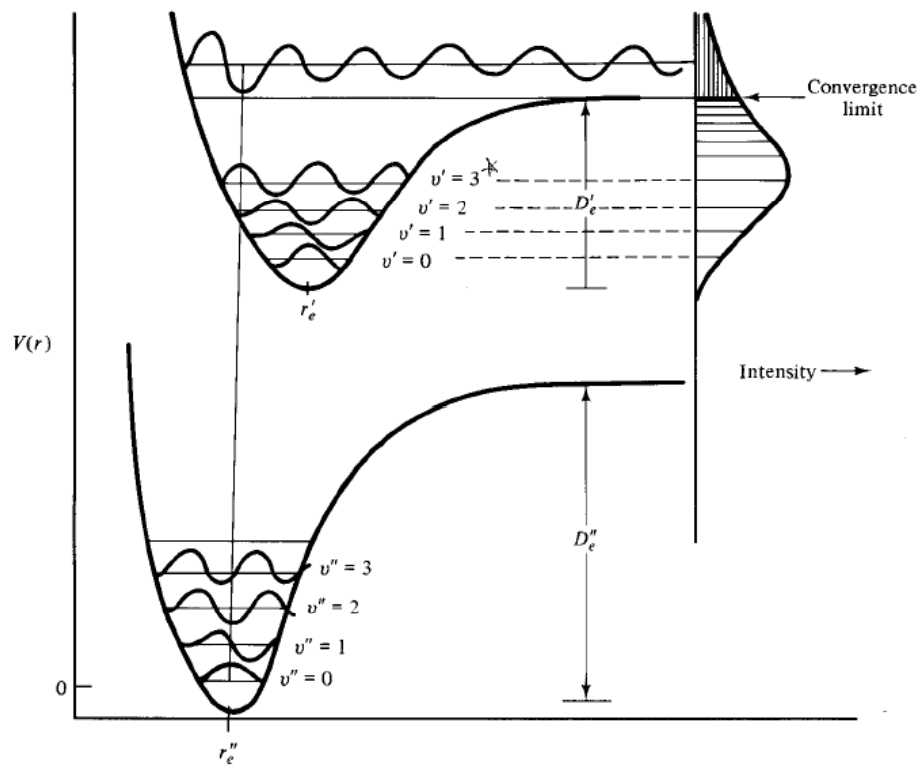


Figure 1.15: Spontaneous emission in a two-level system.

Line shapes: Homogeneous vs inhomogeneous

- Homogeneous line shape:
 - All molecules behave in the same way
 - Lorentz line shape
 - Examples are:

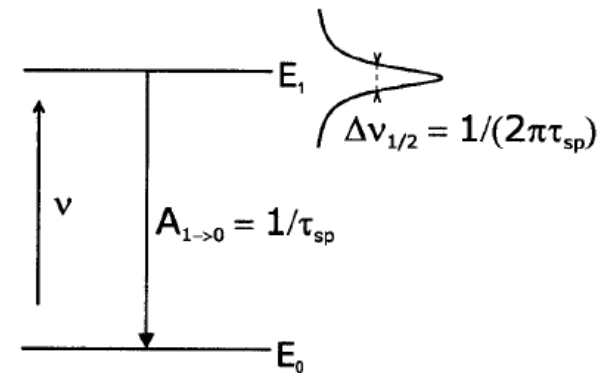
- Pressure broadening
- Natural lifetime broadening
- Transit time broadening

$$\Delta\nu_{1/2} = bp. \quad b=10 \text{ MHz/Torr}$$

$$\tau_{sp} \equiv 1/A_{1 \rightarrow 0} \quad \tau_{sp} = \frac{1}{\sum A_{n \rightarrow j}}$$

Heissenberg's uncertainty principle:

$$\Delta E \Delta t \geq \hbar \quad \text{or} \quad \Delta \nu \Delta t \geq \frac{1}{2\pi}$$



Line shapes (cont): Homogeneous vs inhomogeneous

- Inhomogeneous line shape:
 - All molecules behave differently (distribution)
 - Gaussian line shape
 - Examples are:

- Doppler broadening ————— $\Delta\nu = \frac{v}{c} \left(\frac{2kT \ln 2}{m} \right)^{1/2}$

- Power broadening ————— $\Delta\nu \sim \frac{\mu_{10} E}{2\pi\hbar} = \frac{\omega_R}{4\pi^2}$

Line shapes: Homogeneous vs inhomogeneous

- Homogeneous line shape:
 - All molecules behave in the same way
 - Lorentz line shape
 - Examples are:

- Natural lifetime broadening

$$\tau_{\text{sp}} \equiv 1/A_{1 \rightarrow 0} \quad \tau_{\text{sp}} = \frac{1}{\sum A_{n \rightarrow j}}$$

- (Transit time broadening)

- (Power broadening)

$$\Delta\nu \sim \frac{\mu_{10}E}{2\pi\hbar} = \frac{\omega_R}{4\pi^2}$$

Heisenberg's uncertainty principle:

$$\Delta E \Delta t \geq \hbar \quad \text{or} \quad \Delta\nu \Delta t \geq \frac{1}{2\pi}$$

Lorentzian line shape function

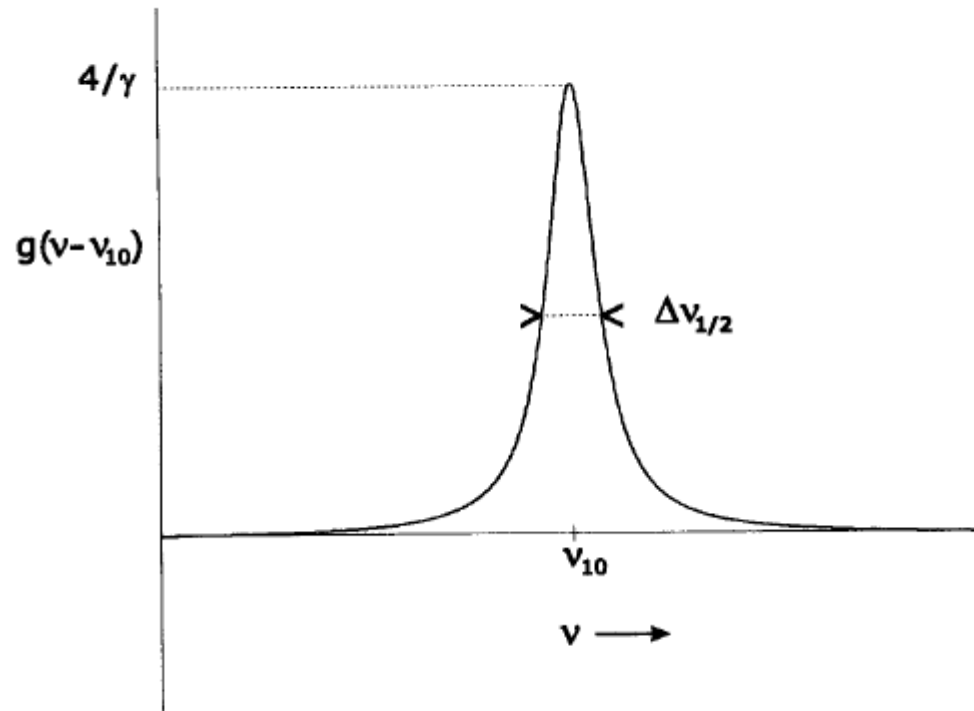
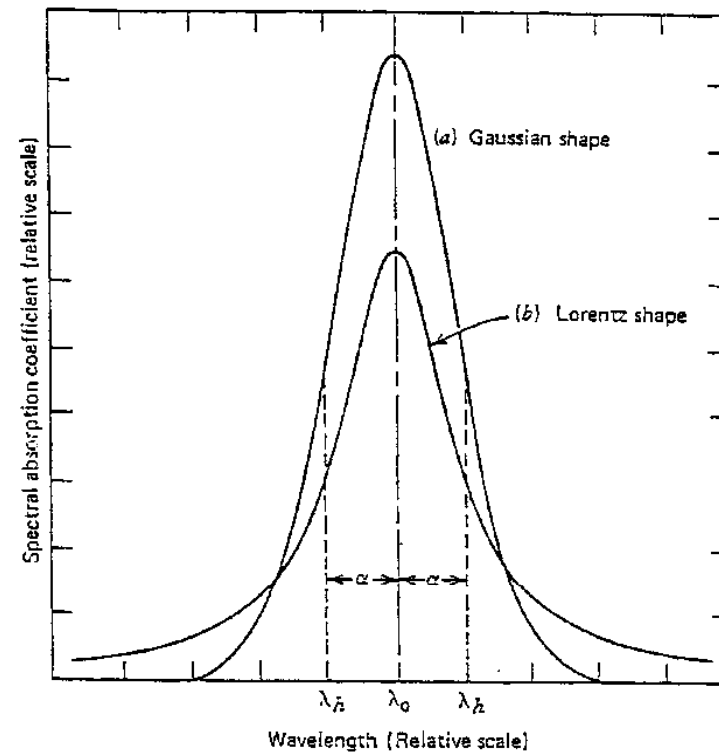


Figure 1.18: A normalized Lorentzian function.

$$g(\nu - \nu_0) = \frac{\Delta\nu_{1/2}/(2\pi)}{(\Delta\nu_{1/2}/2)^2 + (\nu - \nu_0)^2}$$

Gaussian lineshape function



$$g(\nu-\nu_0) = A \exp -[(\nu-\nu_0)^2 / (2 \alpha^2)]$$

Voigt lineshape function

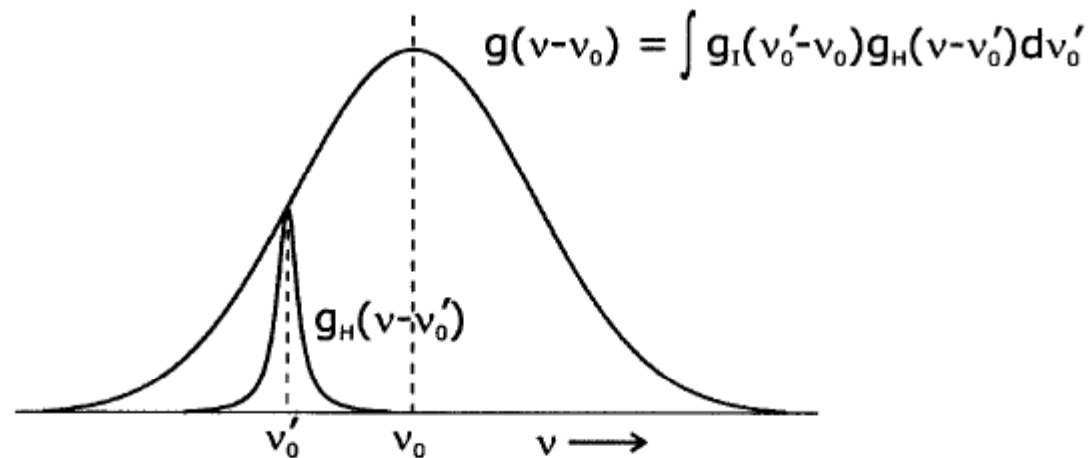


Figure 1.21: The Voigt lineshape is a convolution of an inhomogeneous Gaussian lineshape function with a homogeneous Lorentzian lineshape function.

<http://scienceworld.wolfram.com/physics/topics/SpectralLineshapes.html>

- At what pressure will the Doppler broadening (FWHM) equal the pressure broadening (FWHM) for a room temperature (20C) sample of CO gas for a pure rotational transition at 115 GHz, a vibrational-rotational transition at 2140 cm^{-1} , and an electronic transition at 1537 Å ? Use a “typical” pressure-broadening coefficient of 10 MHz/Torr in all three cases.

Example CO

	115 GHz	2140 cm^{-1}	1537 A
• Doppler	10^{-8} Hz	$5 \cdot 10^{-3}$ cm^{-1}	0.15 cm^{-1}
• Pressure		15 Torr	450 Torr

– $M = 28$ amu

– $T = 20$ C

– $b = 10$ MHz Torr $^{-1} = 3.33 \cdot 10^{-4}$ cm^{-1} Torr $^{-1}$

- The absorption cross section of Mercury atoms is $3.3 \times 10^{-14} \text{ cm}^2$ (measured at 253.65nm with a spectral resolution of 0.015nm). Your instrument is capable of detecting an optical density of 10^{-4} , and measures over a pathlength of 1 m. What Hg concentration is detectable ?
- A: $10^5 < x < 10^6 \text{ molec m}^{-3}$
- B: $10^6 < x < 10^7 \text{ molec m}^{-3}$
- C: $10^7 < x < 10^8 \text{ molec m}^{-3}$
- D: $10^8 < x < 10^9 \text{ molec m}^{-3}$
- E: $> 10^{10} \text{ molec m}^{-3}$