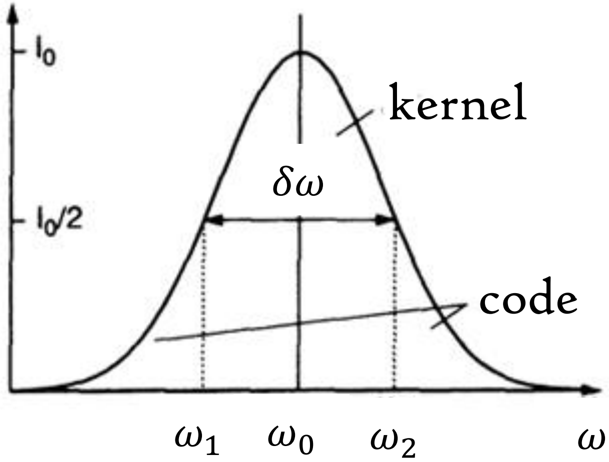
CHAPTER 2

WIDTHS AND PROFILES OF SPECTRAL PROFILES

2.1 NATURAL LINEWIDTH

- Spectral lines in discrete absorption or emission spectra are never strictly monochromatic.
- Even with the very high resolution of interferometers, one observes a spectral distribution $I(v)$ of the absorbed or emitted intensity around the central frequency $\omega_0 = \frac{(E_b - E_a)}{\hbar}$ corresponding to a molecular transition with the energy difference $\Delta E = E_b - E_a$ between upper and lower levels.
- The function $I(\omega)$ in the vicinity of ω_0 is called the **line profile**.
- The frequency interval $\delta\omega = |\omega_2 - \omega_1|$ between the two frequencies ω_2 and ω_1 for which $I(\omega_1) = I(\omega_2) = I(\omega_0)/2$ is the **Full-Width Half-Maximum (FWHM)** of the line, often shortened to the **linewidth**.

The spectral region within the halfwidth is called the **kernel of the line**, the regions outside are the **line wings**.



2.1 NATURAL LINEWIDTH

2.1.1 Lorentzian line profile of emitted radiation

- The spectral line profile of a radiative transition can be determined with a classical model.
- Let's consider to irradiate a sample of molecules with monochromatic radiation resonant with the transition $E_a \rightarrow E_b$.
- Let's consider the spontaneous emission of transition $E_b \rightarrow E_a$. We shall describe the excited atomic electron by the classical model of a damped harmonic oscillator with frequency ω, mass m and restoring force constant k.
  - The radiative energy loss results in a damping of the oscillation described by the damping constant γ.
  - We shall see, however, that for real atoms the damping is extremely small, which means that $\gamma \ll \omega$.

The amplitude $x(t)$ of the oscillation can be obtained by solving the differential equation of motion:

$$\ddot{x}(t) + \gamma\dot{x}(t) + \omega_0^2 x(t) = 0$$

with $\omega_0^2 = \frac{k}{m}$

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2.1.1 Lorentzian line profile of emitted radiation

The real solution of with the initial values $x(0) = x_0$ and $\dot{x}(0) = 0$, is:

$$x(t) = x_0 e^{-\frac{\gamma}{2}t}\left[cos(\omega t) + \frac{\gamma}{2\omega} sen(\omega t)\right]$$

The frequency $\omega = \sqrt{\left(\omega_0^2 - \frac{\gamma^2}{4}\right)}$ of the damped oscillation is slightly lower than the frequency ω_0 of the undamped case.

However, for small damping, we can set $\omega \simeq \omega_0$ nd also may neglect the second term in $x(t)$. With this approximation, which is still very accurate for real atoms, we obtain the solution as

$$x(t) = x_0 e^{-\frac{\gamma}{2}t} cos(\omega_0 t)$$

The frequency $\omega_0 = 2\pi v_0$ of the oscillator corresponds to the central frequency $\omega_{ab} = \frac{E_b - E_a}{\hbar}$ of an atomic transition $E_b \rightarrow E_a$.

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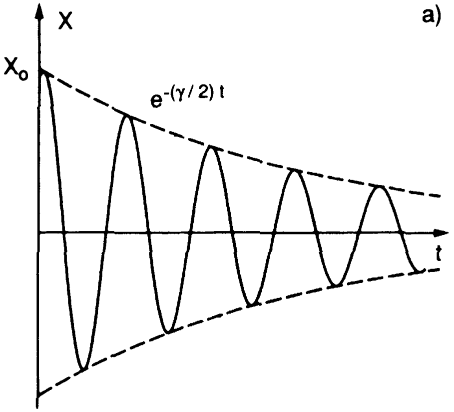
2.1.1 Lorentzian line profile of emitted radiation

Because the amplitude $x(t)$ f the oscillation decreases gradually, the frequency of the emitted radiation is no longer monochromatic as it would be for an oscillation with constant amplitude. Instead, it shows a frequency distribution related to the function $x(t)$ x(t) by a Fourier transformation.



$$x(t) = x_0 e^{-\frac{\gamma}{2}t} cos(\omega_0 t)$$

The damped oscillation $x(t)$ can be described as a superposition of monochromatic oscillations $e^{i\omega t}$ with slightly different frequencies ω and amplitudes $A(\omega)$:

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

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2.1.1 Lorentzian line profile of emitted radiation

The amplitudes $A(\omega)$ are calculated as the Fourier transform:

$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} x(t)\, e^{-i\omega t} dt = \frac{1}{\sqrt{2\pi}} \int_{0}^{\infty} x_0 e^{-\frac{\gamma}{2}t} cos(\omega_0 t)\, e^{-i\omega t} dt$$

$$x(t) = x_0 e^{-\frac{\gamma}{2}t} cos(\omega_0 t)$$

$$x(t) = \frac{1}{2\sqrt{2\pi}} \int_{0}^{\infty} A(\omega)\, e^{i\omega t} d\omega$$

The lower integration limit is taken to be zero because $x(t) = 0\ \forall t > 0$.

The integral can readily be integrated to give the complex amplitudes:

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

The real intensity $I(\omega)$ will be:

$$I(\omega) \propto\ A(\omega) A^{*}(\omega)$$

and contains terms with $(\omega - \omega_0)$ and $(\omega + \omega_0)$ at the denominator

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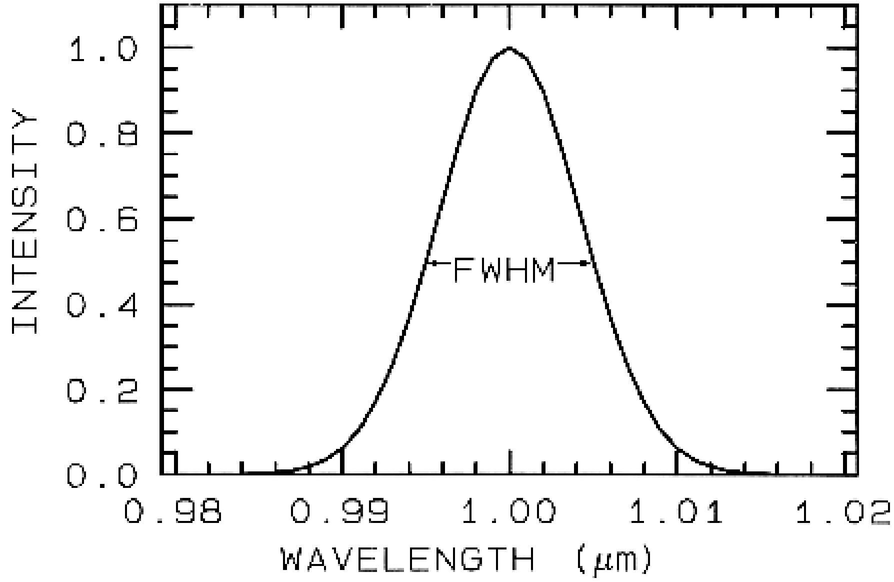
2.1.1 Lorentzian line profile of emitted radiation

In the vicinity of the central frequency ω_0 of an atomic transition where $(\omega - \omega_0)^2 \ll \omega_0^2$ the terms with $(\omega + \omega_0)$ can be neglected.

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

Thus, the intensity profile of the spectral line becomes:

$$I(\omega-\omega_0) = \frac{C}{(\omega-\omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$



2.1 NATURAL LINEWIDTH

2.1.1 Lorentzian line profile of emitted radiation

The constant C can be defined in two different ways:

a) For comparison of different line profiles, it is useful to define a normalized intensity profile $L(\omega-\omega_0)=I(\omega-\omega_0)/I_0$ with $I_0=\int I(\omega)d\omega$ such that:

$$\int_0^{\infty} L(\omega-\omega_0)\,d\omega=\int_{-\infty}^{\infty} L(\omega-\omega_0)\,d(\omega-\omega_0)=1$$

Including the expression $I(\omega-\omega_0)$ one obtains:

$$I(\omega-\omega_0)=\frac{C}{(\omega-\omega_0)^2+\left(\frac{\gamma}{2}\right)^2}$$

$$\int_{-\infty}^{\infty} L(\omega-\omega_0)\,d(\omega-\omega_0)=\int_{-\infty}^{\infty}\frac{I(\omega-\omega_0)}{I_0}\,d(\omega-\omega_0)$$

$$=\frac{1}{I_0}\int_{-\infty}^{\infty}\frac{C}{(\omega-\omega_0)^2+\left(\frac{\gamma}{2}\right)^2}\,d(\omega-\omega_0)=\frac{C}{I_0}\frac{2\pi}{\gamma}=1$$

$$\int_{-\infty}^{\infty}\frac{1}{1+x^2}\,dx=arctgx$$

from which:

$$C=\frac{I_0\gamma}{2\pi}$$

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2.1.1 Lorentzian line profile of emitted radiation

$$L(\omega-\omega_0)=\frac{I(\omega-\omega_0)}{I_0}$$

$$I(\omega-\omega_0)=\frac{C}{(\omega-\omega_0)^2+\left(\frac{\gamma}{2}\right)^2}$$

$$C=\frac{I_0\gamma}{2\pi}$$

So in definitive:

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

is called the **normalized Lorentzian profile**.

We calculate the FWHM. The maximum of the normalized intensity profile at $\omega=\omega_0$ is:

$$L_{MAX}=\frac{1}{2\pi}\frac{\gamma}{\left(\frac{\gamma}{2}\right)^2}=\frac{2}{\pi\gamma}$$

The value of $\omega_F-\omega_0$ with respect to which L is reduced by $L_{MAX}/2$ will be:

$$\frac{L_{MAX}}{2}=\frac{1}{\pi\gamma}=\frac{1}{2\pi}\frac{\gamma}{(\omega_F-\omega_0)^2+\left(\frac{\gamma}{2}\right)^2}$$

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from which:

$$(\omega_F - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2 = \frac{\gamma^2}{2}$$

$$\frac{L_{MAX}}{2} = \frac{1}{\pi\gamma} = \frac{1}{2\pi}\frac{\gamma}{(\omega_F - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$

and so:

$$\omega_F - \omega_0 = \frac{\gamma}{2}$$

The FWHM value will be:

$$2(\omega_F - \omega_0) = \delta\omega = \gamma \qquad \text{or} \qquad \delta\nu = \frac{\gamma}{2\pi}$$

Any intensity distribution with a Lorentzian profile is then:

$$I(\omega - \omega_0) = \frac{I_0}{2\pi}\frac{\gamma}{(\omega - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$

with a peak intensity $I(\omega_0) = \frac{2I_0}{\pi\gamma}$ and $I_0 = \int I(\omega)d\omega$

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2.1.1 Lorentzian line profile of emitted radiation

b) the normalization is chosen in such a way that $I(\omega_0) = I_0$; furthermore, the full halfwidth is denoted by 2Γ. In this notation the line profile:

$$L^*(\omega - \omega_0) = \frac{I(\omega - \omega_0)}{I_0} = \frac{I(\omega - \omega_0)}{I(\omega_0)}$$

Since:

$$I(\omega_0) = \frac{C}{\left(\frac{\gamma}{2}\right)^2}$$

$$I(\omega - \omega_0) = \frac{C}{(\omega - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$

then:

$$L^*(\omega - \omega_0) = \frac{I(\omega - \omega_0)}{\frac{C}{\left(\frac{\gamma}{2}\right)^2}} = \frac{C}{(\omega - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2} \cdot \frac{\left(\frac{\gamma}{2}\right)^2}{C} = \frac{\Gamma^2}{(\omega - \omega_0)^2 + \Gamma^2}$$

with $\Gamma = \frac{\gamma}{2}$

2.1 NATURAL LINEWIDTH

2.1.1 Lorentzian line profile of emitted radiation

Assuming $x = \frac{\omega - \omega_0}{\Gamma}$, $L^*(\omega - \omega_0)$ can be abbreviated as:

$$L^*(\omega - \omega_0) = \frac{1}{1 + x^2}$$

$$L^*(\omega - \omega_0) = \frac{\Gamma^2}{(\omega - \omega_0)^2 + \Gamma^2}$$

with $L^*(\omega_0) = 1$

In this notation the area under the line profile becomes:

$$\int_0^\infty I(\omega)\, d\omega = \Gamma \int_{-\infty}^{\infty} I(x)\, dx = I_0 \Gamma \pi$$

2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

The radiant power of the damped oscillator can be obtained from if both sides of the equation $\dot{x}(t)$ are multiplied by $m\dot{x}(t)$:

$$\ddot{x}(t) + \gamma\dot{x}(t) + \omega_0^2 x(t) = 0$$

$$m\ddot{x}(t)\dot{x}(t) + m\omega_0^2 x(t)\dot{x}(t) = -\gamma m\dot{x}(t)^2$$

Recalling that the kinetic energy for an oscillator is equal to $m\dot{x}(t)^2/2$ and its potential energy is equal a $m\omega_0^2 x^2/2$, then the expression can be rewritten as:

$$\frac{d}{dt}\left(\frac{m}{2}\dot{x}(t)^2 + \frac{m}{2}\omega_0^2 x^2\right) = \frac{dW}{dt} = -\gamma m\dot{x}(t)^2$$

Includgin the expression derived for $x(t) = x_0 e^{-\frac{\gamma}{2}t} cos(\omega_0 t)$ and neglecting the terms proportional to γ^2:

$$\frac{dW}{dt} = -\gamma m x_0^2 \omega_0^2 e^{-\gamma t} sen^2(\omega_0 t)$$

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2.1.2 Relation Between Linewidth and Lifetime

Because the time average: $\overline{sen^2(\omega_0 t)} = \frac{1}{2}$ the time-averaged radiant power:

$$\frac{dW}{dt} = -\gamma m x_0^2 \omega_0^2 e^{-\gamma t} sen^2(\omega_0 t)$$

$$\frac{\overline{dW}}{dt} = -\frac{\gamma}{2} m x_0^2 \omega_0^2 e^{-\gamma t}$$

Equation shows that $\frac{\overline{dW}}{dt}$ decreases to $1/e$ of its initial value after the decay time $\tau = 1/\gamma$.

Previously we saw that the mean lifetime τ_i of a molecular level E_i which decays exponentially by spontaneous emission, is related to the Einstein coefficient A_i by the relation $\tau_i = 1/A_i$.

Replacing the classical damping constant γ by the spontaneous transition probability A_i, we can use the classical formula

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

$$L(\omega - \omega_0) = \frac{1}{2\pi} \frac{A_i}{(\omega - \omega_0)^2 + \left(\frac{A_i}{2}\right)^2}$$

2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

as a correct description of the frequency distribution of spontaneous emission and its linewidth. The natural halfwidth of a spectral line spontaneously emitted from the level E_i is

$$\delta\omega = A_i \quad \text{or} \quad \delta\nu = \frac{A_i}{2\pi}$$

$$\delta\omega = \gamma$$

The radiant power emitted from N_i excited atoms on a transition $E_i \rightarrow E_k$ is given by:

$$\frac{dW_{ik}}{dt} = N_i A_{ik} \hbar\omega_{ik}$$

If the emission of a source with volume ΔV is isotropic, the radiation power received by a detector of area A at a distance r through the solid angle $d\Omega = A/r^2$ is:

$$P_{ik} = \left(\frac{dW_{ik}}{dt}\right)\frac{d\Omega}{4\pi} = N_i A_{ik} \hbar\omega_{ik} \Delta V \frac{A}{4\pi r^2}$$

This means that the density N_i of emitters can be inferred from the measured power, if A_{ik} is known.

2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

In a similar way, the spectral profile of an absorption line can be derived for atoms at rest. The intensity I of a plane wave passing in the z-direction through an absorbing sample decreases along the distance dz :

$$dI = -\alpha I dz$$

$$dP_{ik}(\omega)d\omega = P_0(\omega)\left(N_i - \frac{g_i}{g_k}N_k\right)\sigma_{ik}Adxd\omega$$

The absorption coefficient α_{ik} $[cm^{-1}]$ for a transition $|i\rangle \rightarrow |k\rangle$ depends on population densities N_i and N_k of the lower and upper level, respectively, and on the optical absorption cross section σ_{ik} $[cm^2]$ of each absorbing atom:

$$\alpha_{ik}(\omega) = \sigma_{ik}(\omega)\left(N_i - \frac{g_i}{g_k}N_k\right)$$

which reduces to $\alpha_{ik}(\omega) = \sigma_{ik}N_i$ when $N_k \ll N_i$. For sufficiently small intensities I, the induced absorption rate is small compared to the refilling rate of level $|i\rangle$ and the population density N_i does not depend on the intensity I.

2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

Integration of the equation then yields **Lambert-Beer's law**

$$I = I_0 e^{-\alpha(\omega)z}$$

$dI = -\alpha I dz$

The absorption profile $\alpha(\omega)$ can be obtained from our classical model of a damped oscillator with charge q under the influence of a driving force qE caused by the incident wave with amplitude $E = E_0 e^{i\omega t}$. The corresponding differential equation in 1D:

$$m\ddot{x}(t) + b\dot{x}(t) + kx(t) = qE_0 e^{i\omega t}$$

has the solution:

$$x(t) = \frac{qE_0 e^{i\omega t}}{m(\omega_0^2 - \omega^2 + i\gamma\omega)}$$

with $\gamma = b/m$ and $\omega_0^2 = k/m$.

2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

The forced oscillation of the charge q generates an induced dipole moment:

$$p(t) = qx(t) = \frac{q^2 E_0 e^{i\omega t}}{m(\omega_0^2 - \omega^2 + i\gamma\omega)}$$

In a sample with N oscillators per unit volume, the macroscopic polarization P, which is the sum of all dipole moments per unit volume, is therefore:

$$P = Nqx(t)$$

On the other hand, the polarization can be derived in classical electrodynamics from Maxwell’s equations using the dielectric constant ε_0, i.e.:

$$\boldsymbol{P} = \varepsilon_0(\varepsilon - 1)\boldsymbol{E}$$

and using Maxwell's equations it is possible to derive the relationship between refractive index n and relative dielectric constant ε:

$$v = \frac{1}{\sqrt{\varepsilon\varepsilon_0\mu\mu_0}} = \frac{c}{n}$$

2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

Since $c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}$, then $n = \sqrt{\varepsilon\mu}$

Except for ferromagnetic materials, the relative permeability is $\mu \simeq 1$, leading to:

$$n = \sqrt{\varepsilon}$$

We combine the latest expressions found:

$$\frac{P}{E} = \frac{Nqx(t)}{E} = \frac{Nq^2}{m(\omega_0^2 - \omega^2 + i\gamma\omega)}$$ Harmonic oscillator

$$\frac{P}{E} = \varepsilon_0(\varepsilon - 1) = \varepsilon_0(n^2 - 1)$$ Maxwell's equation

and get:

$$n^2 = 1 + \frac{Nq^2}{\varepsilon_0 m(\omega_0^2 - \omega^2 + i\gamma\omega)}$$

2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

In gaseous media at sufficiently low pressures, the index of refraction is close to unity (for example, in air at atmospheric pressure, n = 1.00028 for λ = 500 nm). In this case, the approximation:

$$n^2 - 1 = (n+1)(n-1) \simeq 2(n-1)$$

leads to:

$$n = 1 + \frac{Nq^2}{2\varepsilon_0 m(\omega_0^2 - \omega^2 + i\gamma\omega)}$$

$$n^2 = 1 + \frac{Nq^2}{\varepsilon_0 m(\omega_0^2 - \omega^2 + i\gamma\omega)}$$

In order to make clear the physical implication of this complex index of refraction, we separate the real and the imaginary parts and write:

$$n = n' - i\kappa$$

It is therefore necessary to separate the real part and the imaginary part of the expression found of the refractive index:

2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

We multiply and divide by the complex conjugate of the denominator:

$$n = 1 + \frac{Nq^2}{2\varepsilon_0 m}\left[\left(\frac{1}{\omega_0^2 - \omega^2 + i\gamma\omega}\right)\frac{(\omega_0^2 - \omega^2) - i\gamma\omega}{(\omega_0^2 - \omega^2) - i\gamma\omega}\right]$$

$$= 1 + \frac{Nq^2}{2\varepsilon_0 m}\left[\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} - i\,\frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}\right]$$

$$n = 1 + \frac{Nq^2}{2\varepsilon_0 m(\omega_0^2 - \omega^2 + i\gamma\omega)}$$

And so:

$$n' = 1 + \frac{Nq^2}{2\varepsilon_0 m}\frac{\omega_0^2 - \omega^2}{\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2}$$

$$k = \frac{Nq^2}{2\varepsilon_0 m}\frac{\gamma\omega}{\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2}$$

These equations are known as **Kramers–Kronig dispersion relations**.

2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

An EM wave $E = E_0 e^{i(\omega t - kz)}$ passing in the z-direction through a medium with the refractive index n has the same frequency ω as in vacuum, but a different wave vector $k = k_0 n$. Inserting $|k| = 2\pi/\lambda$ and $n = n' - i\kappa$ yields

$$E = E_0 e^{i(\omega t - n k_0 z)} = E_0 e^{i(\omega t - n' k_0 z + i k_0 \kappa z)}$$
$$= E_0 e^{-k_0 \kappa z} e^{i(\omega t - n' k_0 z)} = E_0 e^{-\frac{2\pi\kappa z}{\lambda}} e^{i k_0 (ct - n' z)}$$

$n = n' - i\kappa$
$|k| = 2\pi/\lambda$

Equation (3.33) shows that the imaginary part $\kappa(\omega)$ of the complex refractive index n describes the **absorption of the EM wave**.

At a penetration depth of $\Delta z = \frac{\lambda}{2\pi\kappa}$, the amplitude $E_0 e^{-\frac{2\pi\kappa z}{\lambda}}$ has decreased to $1/e$ of its initial value.

The real part $n'(\omega)$ represents the **dispersion of the EM wave**, i.e., the dependence of the phase velocity $v(\omega) = c/n'(\omega)$ on the frequency.

2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

The intensity of the wave will then be equal to:

$$E = E_0 e^{-\frac{2\pi\kappa z}{\lambda}} e^{ik_0(ct-n'z)}$$

$$k_0 = \frac{2\pi}{\lambda}$$

$$I = EE^* = I_0 e^{-2k_0\kappa z}$$

Comparing it with the Lambert-Beer law, we get:

$$I = I_0 e^{-\alpha(\omega)z}$$

$$\alpha = 2k_0\kappa = \frac{4\pi\kappa}{\lambda_0}$$

The absorption coefficient α is proportional to the imaginary part κ of the refractive index. Using the Kramers-Kronig relations, one obtains ($q = e$)

$$\alpha = \frac{4\pi N e^2}{2\lambda_0\varepsilon_0 m}\frac{\gamma\omega}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}$$

$$k = \frac{Nq^2}{2\varepsilon_0 m}\frac{\gamma\omega}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}$$

Since: $\lambda_0 = \dfrac{2\pi c}{\omega_0}$

$$\alpha = \frac{Ne^2\omega_0}{c\varepsilon_0 m}\frac{\gamma\omega}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}$$

2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

In the neighborhood of a molecular transition frequency ω_0, where $|\omega_0 - \omega| \ll \omega_0$, the dispersion relations reduce:

$$\alpha = \frac{Ne^2\omega_0}{c\varepsilon_0 m}\frac{\gamma\omega}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2} = \frac{Ne^2\omega_0}{c\varepsilon_0 m}\frac{\gamma\overset{\sim\omega_0}{\omega}}{[(\omega_0-\omega)\underbrace{(\omega_0+\omega)}_{\sim 2\omega_0}]^2+\gamma^2\overset{\sim\omega_0^2}{\omega^2}}$$

$$\approx \frac{Ne^2\omega_0}{4c\varepsilon_0 m}\frac{\gamma\omega_0}{\omega_0^2(\omega_0-\omega)^2+\left(\frac{\gamma}{2}\right)^2\omega_0^2} = \frac{Ne^2}{4\varepsilon_0 mc}\frac{\gamma}{(\omega_0-\omega)^2+\left(\frac{\gamma}{2}\right)^2}$$

The same for the real part n' :

$$n' = 1 + \frac{Nq^2}{2\varepsilon_0 m}\frac{\omega_0^2-\omega^2}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2} = 1 + \frac{Nq^2}{2\varepsilon_0 m}\frac{(\omega_0-\omega)(\omega_0+\omega)}{[(\omega_0-\omega)(\omega_0+\omega)]^2+\gamma^2\omega^2}$$

$$\approx 1 + \frac{Nq^2}{2\varepsilon_0 m}\frac{(\omega_0-\omega)\omega_0}{[(\omega_0-\omega)\omega_0]^2+\gamma^2{\omega_0}^2} = 1 + \frac{Nq^2}{2\varepsilon_0 m\omega_0}\frac{(\omega_0-\omega)}{(\omega_0-\omega)^2+\gamma^2}$$

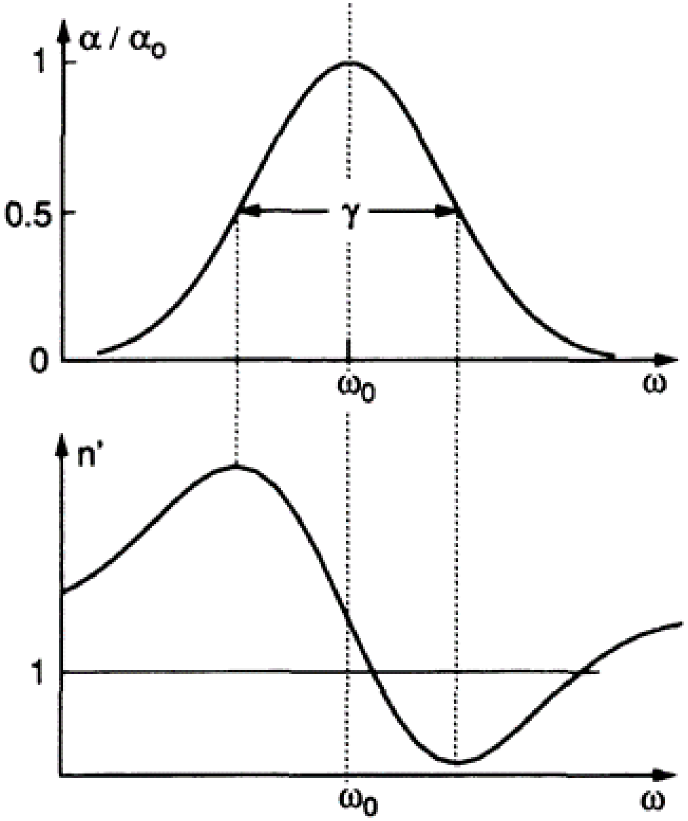
2.1 NATURAL LINEWIDTH

2.1.2 Relation Between Linewidth and Lifetime

Finally, the **Kramers-Kronig dispersion** relations become:

$$\alpha = \frac{Ne^2}{4\varepsilon_0 mc} \frac{\left(\frac{\gamma}{2}\right)}{(\omega_0 - \omega)^2 + \left(\frac{\gamma}{2}\right)^2}$$

$$n' = 1 + \frac{Ne^2}{4\varepsilon_0 m\omega_0} \frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + \left(\frac{\gamma}{2}\right)^2}$$



The spectral absorption profile $\alpha(\omega)$ is Lorentzian with a FWHM equal to $\Delta\omega = \gamma$, which equals the natural linewidth.

2.2 DOPPLER WIDTH

- Generally, the Lorentzian line profile with the natural linewidth cannot be observed without special techniques, because it is completely concealed by other broadening effects.

- One of the major contributions to the spectral linewidth in gases at low pressures is the **Doppler width**, which is due to the thermal motion of the absorbing or emitting molecules.

Consider an excited molecule with a velocity $\boldsymbol{v} = \{v_x, v_{y,} v_z\}$ relative to the rest frame of the observer. The central frequency of a molecular emission line that is ω_0 in the coordinate system of the molecule is Doppler shifted to:

$$\omega_e = \omega_0 + \boldsymbol{k} \cdot \boldsymbol{v}$$

for an observer looking toward the emitting molecule (that is, against the direction of the wave vector $\boldsymbol{k}$ of the emitted radiation.

2.2 DOPPLER WIDTH

- For the observer, the apparent emission frequency ω_e is increased if the molecule moves toward the observer ($\boldsymbol{k} \cdot \boldsymbol{v} > 0$) and decreased if the molecule moves away ($\boldsymbol{k} \cdot \boldsymbol{v} < 0$).

$$\omega_e = \omega_0 + \boldsymbol{k} \cdot \boldsymbol{v}$$

THE SAME GOES FOR A MOLECULE THAT ABSORBS RADIATION

- Similarly, one can see that the absorption frequency ω_0 of a molecule moving with the velocity $\boldsymbol{v}$ across a plane EM wave $\boldsymbol{E} = \boldsymbol{E_0} e^{i\omega t - \boldsymbol{k} \cdot \boldsymbol{r}}$ is shifted.

The wave frequency ω in the rest frame appears in the frame of the moving molecule as:

$$\omega' = \omega - \boldsymbol{k} \cdot \boldsymbol{v}$$

The molecule can only absorb if ω'coincides with its eigenfrequency ω_0. The absorption frequency $\omega = \omega_a$ will be:

$$\omega_a = \omega_0 + \boldsymbol{k} \cdot \boldsymbol{v}$$

2.2 DOPPLER WIDTH

As in the emission case, the absorption frequency ω_a is increased for $\boldsymbol{k} \cdot \boldsymbol{v} > 0$. This happens, for example, if the molecule moves parallel to the wave propagation.
It is decreased if $\boldsymbol{k} \cdot \boldsymbol{v} < 0$, e.g., when the molecule moves against the light propagation..

$$\omega_a = \omega_0 + \boldsymbol{k} \cdot \boldsymbol{v}$$

If we choose the z −direction to coincide with the light propagation, with $\boldsymbol{k} = \{0,0,k_z\}$ and $|k| = \frac{\omega_0}{c}$, then $\omega_a = \omega_0 + \boldsymbol{k} \cdot \boldsymbol{v}$ becomes:

$$\omega_a = \omega_0 \left(1 + \frac{v_z}{c}\right)$$

At thermal equilibrium, the molecules of a gas follow a Maxwellian velocity distribution. At the temperature T, the number of molecules $n_i(z) dv_z$ per unit volume than in the energy level E_i have a velocity component between v_z and $v_z + dv_z$ is:

2.2 DOPPLER WIDTH

$$n_i(z)dv_z = \frac{N_i}{v_p\sqrt{\pi}} e^{-\left(\frac{v_z}{v_p}\right)^2} dv_z$$

where $N_i = \int n_i(z)dv_z$ s the density of all molecules in level E_i, $v_p = \sqrt{\frac{2KT}{m}}$ is the most probable velocity, m is the mass of the molecule and K is Boltzmann's constant.

Using the relationship $\omega_a = \omega_0\left(1 + \frac{v_z}{c}\right)$, the differential dv_z can be expressed as $dv_z = \frac{c}{\omega_0} d\omega$.

Substituting in the above expression, we obtain the number of molecules with absorption frequencies shifted from ω_0 into the interval $[\omega, \omega + d\omega]$:

$$n_i(\omega)d\omega = N_i \frac{c}{\omega_0 v_p\sqrt{\pi}} e^{-\left[\frac{c(\omega-\omega_0)}{\omega_0 v_p}\right]^2} d\omega$$

2.2 DOPPLER WIDTH

Since the emitted or absorbed radiant power $P(\omega)d\omega$ is proportional to density $n_i(\omega)d\omega$ f molecules emitting or absorbing in the interval $d\omega$, the intensity profile of a Doppler-broadened spectral line becomes:

$$n_i(\omega)d\omega = N_i \frac{c}{\omega_0 v_p \sqrt{\pi}} e^{-\left[\frac{c(\omega-\omega_0)}{\omega_0 v_p}\right]^2} d\omega$$

$$I(\omega) = I_0 e^{-\left[\frac{c(\omega-\omega_0)}{\omega_0 v_p}\right]^2}$$

This is a Gaussian profile. Calculate the FWHM. Being I_0 the maximum power value at $\omega = \omega_0$, the frequency ω^* at which corresponds an intensity equal to $I_0/2$ is:

$$\frac{I_0}{2} = I_0 e^{-\left[\frac{c(\omega^*-\omega_0)}{\omega_0 v_p}\right]^2}$$

After a few mathematical steps you get:

$$\omega^* = \omega_0 + \frac{\omega_0 v_p}{c}\sqrt{ln2}$$

2.2 DOPPLER WIDTH

Then the FWHM of the profile will be:

$$\delta\omega_D = 2\sqrt{ln2}\frac{\omega_0 v_p}{c}$$

Since for a Maxwell distribution, the most probable velocity v_p is given by:

$$v_p = \sqrt{\frac{2KT}{m}}$$

the FWHM of the profile becomes:

$$\delta\omega_D = \left(\frac{\omega_0}{c}\right)\sqrt{\frac{8KTln2}{m}}$$

known as **Doppler width**.

The Doppler width is much larger than the natural linewidth .

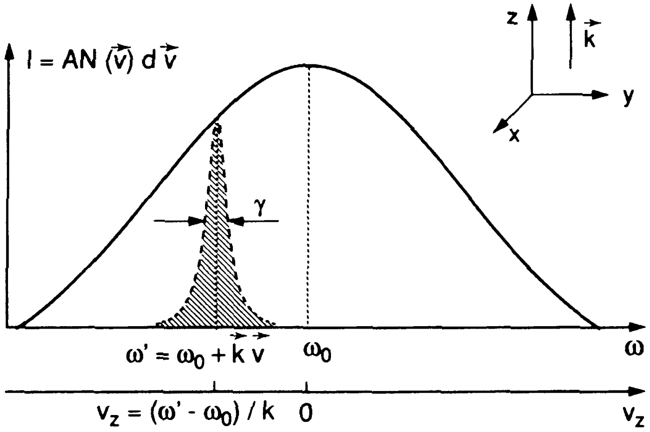
2.2 DOPPLER WIDTH

More detailed consideration shows that a Doppler-broadened spectral line cannot be strictly represented by a pure Gaussian profile as has been assumed in the foregoing discussion, since not all molecules with a definite velocity component v_z emit or absorb radiation at the same frequency $\omega_a = \omega'\left(1 + \frac{v_z}{c}\right)$.

Because of the finite lifetimes of the molecular energy levels, the frequency response of these molecules is represented by a Lorentzian profile:

$$L(\omega - \omega') = \frac{1}{2\pi} \frac{\gamma}{(\omega - \omega')^2 + \left(\frac{\gamma}{2}\right)^2}$$

with a central frequency ω'.



2.2 DOPPLER WIDTH

Let $n(\omega')d\omega' = n(v_z)dv_z$ be the number of molecules per unit volume with velocity components within the interval $[v_z, v_z + dv_z]$.

The spectral intensity distribution $I(\omega)$ of the total absorption or emission of all molecules at the transition $E_i \rightarrow E_k$ is then:

$$I(\omega) = I_0 \int n(\omega')L(\omega - \omega')d\omega'$$

$$L(\omega - \omega') = \frac{1}{2\pi}\frac{\gamma}{(\omega - \omega')^2 + \left(\frac{\gamma}{2}\right)^2}$$

$$n_i(\omega)d\omega = N_i \frac{c}{\omega_0 v_p \sqrt{\pi}} e^{-\left[\frac{c(\omega-\omega_0)}{\omega_0 v_p}\right]^2} d\omega$$

Substituting expressions for $n(\omega')d\omega'$and $L(\omega - \omega')$, we obtain:

$$I(\omega) = C \int_0^\infty \frac{e^{-\left[\frac{c(\omega-\omega_0)}{\omega_0 v_p}\right]^2}}{(\omega - \omega')^2 + \left(\frac{\gamma}{2}\right)^2}$$

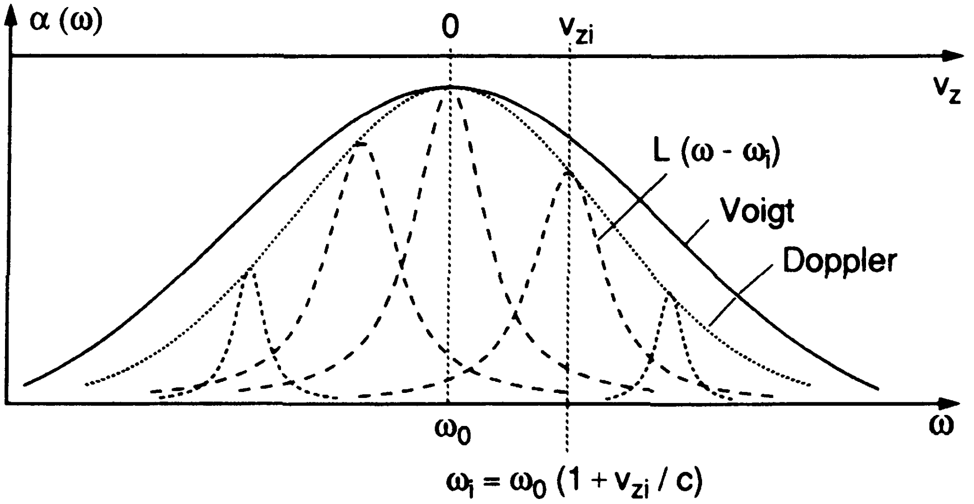
with:

$$C = \frac{\gamma N_i c}{2 v_p \pi^{3/2} \omega_0}$$

2.2 DOPPLER WIDTH

This intensity profile, which is a convolution of Lorentzian and Gaussian profiles, is called a **Voigt profile**. Voigt profiles play an important role in the spectroscopy of stellar atmospheres, where accurate measurements of line wings allow the contributions of Doppler broadening and natural linewidth or collisional line broadening to be separated. From such measurements the temperature and pressure of the emitting or absorbing layers in the stellar atmospheres may be deduced.

$$I(\omega) = C\int_0^\infty \frac{e^{-\left[\frac{c(\omega-\omega_0)}{\omega_0 v_p}\right]^2}}{(\omega-\omega')^2+\left(\frac{\gamma}{2}\right)^2}$$



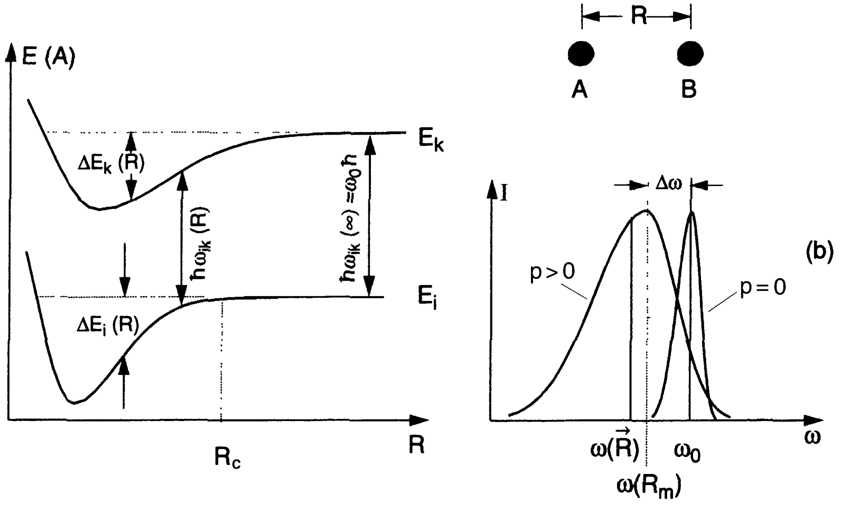
2.3 COLLISIONAL BROADENING

When an atom A with energy levels E_i and E_k approaches another atom or molecule B, the energy levels of A are shifted because of the interaction between A and B.

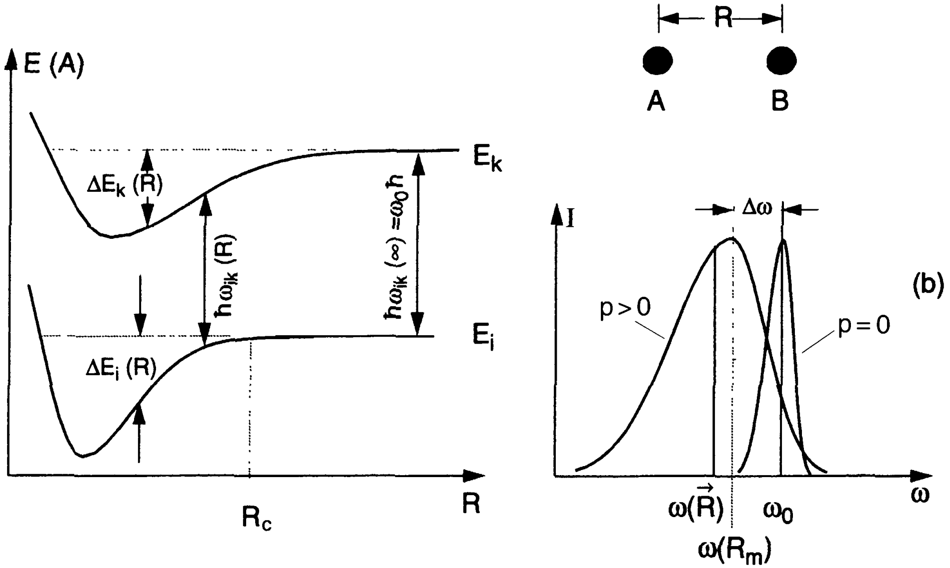
This shift depends on the electron configurations of A and B and on the distance $R(A, B)$, between both collision partners, which we define as the distance between the centers of mass of A and B.

The energy shifts ΔE are, in general, different for the levels E_i and E_k and may be positive as well as negative. The energy shift ΔE is positive if the interaction between A and B is repulsive, and negative if it is attractive.

When plotting the energy $E(R)$ for the two energy levels E_i and E_k as a function of the interatomic distance R, you then get the typical trend in the following Figure.



2.3 COLLISIONAL BROADENING



This mutual interaction of both partners at distances $R < R_C$ is called a collision and radius R_C is the collision radius.

If no internal energy of the collision partners is transferred during the collision by nonradiative transitions, the collision is termed **elastic**.

Without additional stabilizing mechanisms (recombination), the partners will separate again after the collision time $\tau_c \simeq \frac{R_C}{v}$ which depends on the relative velocity v.

2.3 COLLISIONAL BROADENING

2.3.1 Phenomenological description

If atom A undergoes a radiative transition between levels E_i and E_k during the collision time, the frequency :

$$\omega_{ik} = \frac{E_i(R) - E_k(R)}{\hbar}$$

of absorbed or emitted radiation depends on the distance $R(t)$ at the time of the transition.

- We assume that the radiative transition takes place in a time interval that is short compared to the collision time, so that the distance R does not change during the transition. In the previous Figure, this assumption leads to vertical radiative transitions.

In a gas mixture of atoms A and B, the mutual distance $R(A,B)$ shows random fluctuations with a distribution around a mean value $\boldsymbol{R}$ that depends on pressure and temperature.

The fluorescence yields a corresponding frequency distribution around a most probable value $\omega_{ik}(R_m)$ which may be shifted against the frequency ω_0 of the unperturbed atom A.

2.3 COLLISIONAL BROADENING

2.3.1 Phenomenological description

The shift $\Delta\omega = \omega_0 - \omega_{ik}$ depends on how differently the two energy levels E_i and E_k are shifted at a distance$R_m(A, B)$ where the emission probability has a maximum.

The intensity profile $I(\omega)$ of the collision-broadened and shifted emission line can be obtained from:

$$I(\omega) \propto \int A_{ik}(R) P_{col}(R)[E_i(R) - E_k(R)]\, dR$$

where $A_{ik}(R)$ is the spontaneous transition probability, which depends on R because the electronic wave functions of the collision pair (AB) depend on R, and $P_{col}(R)$ is the probability per unit time that the distance between A and B lies in the range from R to $R + dR$.

It follows that the intensity profile of the collision-broadened line reflects the difference of the potential curves:

$$E_i(R) - E_k(R) = V[A(E_i), B] - V[A(E_k), B]$$

2.3 COLLISIONAL BROADENING

2.3.1 Phenomenological description

- Let $V(R)$ be the interaction potential between the ground-state atom A and its collision partner B.
- The probability that B has a distance between R e $R + dR$ will be proportional to $4\pi R^2 dR$ and at thermal equilibrium to the Boltzmann factor $e^{-\frac{V(R)}{KT}}$.
- The number $N(R)$ f collision partners B with distance R from A is therefore:

$$N(R)dR = \mathrm{N}_0 4\pi R^2 e^{-\frac{V(R)}{KT}} dR$$

where N_0 is the average density of atoms B.

Because the intensity of an absorption line is proportional to the density of absorbing atoms while they are forming collision pairs, the intensity profile of the absorption line can be written as:

$$I(\omega)d\omega \propto R^2 e^{-\frac{V(R)}{KT}} d\omega$$

2.3 COLLISIONAL BROADENING

2.3.1 Phenomenological description

We rewrite the differential $d\omega$ from:

$$\hbar\omega_{ik}(R) = E_i(R) - E_k(R) = V_i(R) - V_k(R)$$

Differentiating from R :

$$\hbar\frac{d\omega_{ik}}{dR}dR = \frac{d\big(V_i(R) - V_k(R)\big)}{dR}dR$$

from which substituting in the previous relation:

$$I(\omega)d\omega \propto R^2 e^{-\frac{V(R)}{KT}} d\omega$$

$$I(\omega)d\omega \propto R^2 e^{-\frac{V(R)}{KT}} \frac{d}{dR}[V_i(R) - V_k(R)]dR$$

Typically, several models of spherical potential are substituted for $V(R)$, such as the **Lennard-Jones potential**:

$$V(R) = \frac{a}{R^{12}} - \frac{b}{R^6}$$

The coefficients a and b are adjusted for optimum agreement between theory and experiment.

2.3 COLLISIONAL BROADENING

2.3.2 Inelastic collisions

Besides elastic collisions, inelastic collisions may also occur in which the excitation energy E_i of atom A is either partly or completely transferred into internal energy of the collision partner B, or into translational energy of both partners.

Such inelastic collisions are often called quenching collisions because they decrease the number of excited atoms in level E_i and therefore quench the fluorescence intensity.

The total transition probability A_i for the depopulation of level E_i is a sum of radiative and collision-induced probabilities:

$$A_i = A_i^{rad} + A_i^{coll}$$

with

$$A_i^{coll} = N_B \sigma_B \bar{v}$$

as seen in **CHAPTER 1**

2.3 COLLISIONAL BROADENING

2.3.2 Inelastic collisions

Inserting the relations at the thermal equilibrium:

$$\bar{v} = \sqrt{\frac{8KT}{\pi\mu}}$$

with $\mu = \frac{M_A M_B}{M_A + M_B}$ and $p_B = N_B K T$

between the mean relative velocity v, the pressure p_B and the gas temperature T, we have that the total transition probability becomes:

$$A_i = \frac{1}{\tau_{sp}} + a p_B$$

con $a = 2\sigma_B \sqrt{\frac{2}{\pi\mu KT}}$

$$A_i = {A_i}^{rad} + {A_i}^{coll}$$

$$ {A_i}^{coll} = N_B \sigma_B \bar{v}$$

It is evident that the transition probability is pressure-dependent.

In the paragraph **2.1.2 Relation Between Linewidth and Lifetime** we have shown that the natural linewidth $\delta\omega_n$ coincides with the transition probability A_i.

2.3 COLLISIONAL BROADENING

2.3.2 Inelastic collisions

It follows that this pressure-dependent transition probability causes a corresponding pressure-dependent linewidth $\delta\omega$, which can be described by a sum of two damping terms:

$$\delta\omega = \delta\omega_n + \delta\omega_{coll} = \gamma_n + \gamma_{coll} = \gamma_n + ap_B$$

$$A_i = \frac{1}{\tau_{sp}} + ap_B$$

The collision-induced additional line broadening ap_B is therefore often called **pressure broadening**.

Considering the expression of the line profile previously obtained, it follows that the inelastic collisions contribute to broad the line profile with a FWHM $\gamma = \gamma_n + \gamma_{coll}$:

$$I(\omega - \omega_0) = \frac{C}{(\omega - \omega_0)^2 + \left(\frac{\gamma_n + \gamma_{coll}}{2}\right)^2}$$

$$I(\omega - \omega_0) = \frac{C}{(\omega - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$

2.3 COLLISIONAL BROADENING

2.3.2 Inelastic collisions

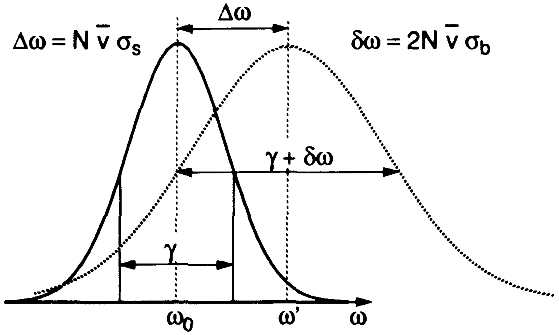
The discussion showed how both elastic and inelastic collisions cause a spectral broadening of the line profile.

Elastic collisions also cause a peak shift that depends on potential curves $E_i(R)$ and $E_k(R)$.

Ultimately, we can write the line profile as:

$$I(\omega-\omega_0)=\frac{I_0}{2\pi}\frac{\frac{\gamma}{2}+N_B\sigma_B\bar{v}}{(\omega-\omega_0-N_B\sigma_s\bar{v})^2+\left(\frac{\gamma}{2}+N_B\sigma_B\bar{v}\right)^2}$$

where the shift $N_B\sigma_s\bar{v}$ and the broadening $N_B\sigma_B\bar{v}$of the line profile are determined by the number density N_B of collisional partner B and by the collision cross sections σ_s for the line shift, and σ_B for broadening



This Lorentzian profile that takes into account the phenomena of collision must be used for the convolution with the Gaussian profile due to Doppler broadening to derive the Voigt profile of the absorption line.

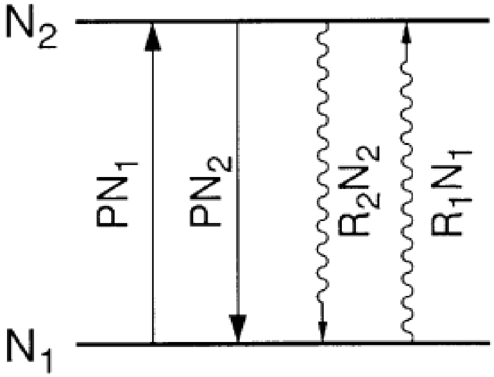
2.3 SATURATION AND POWER BROADENING

At sufficiently large laser intensities, the optical pumping rate on an absorbing transition becomes larger than the relaxation rates.

This results in a noticeable decrease of the population in the absorbing levels. This saturation of the population densities also causes additional line broadening.

The effect of optical pumping on the saturation of population densities is illustrated by a two-level system with population densities N_1 and N_2.

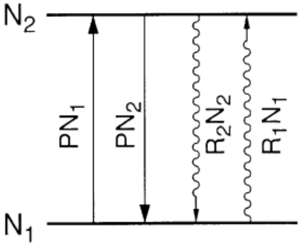
The two levels are coupled to each other by absorption or emission and by relaxation processes, but have no transitions to other levels.



2.3 SATURATION AND POWER BROADENING

With the probability $P = \mathcal{B}_{12}\rho(\omega)$ for a transition $|1\rangle \rightarrow |2\rangle$ by absorption of photons $\hbar\omega$ and the relaxation probability R_i for level $|i\rangle$, the rate equation for the level population is:

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt} = -PN_1 - R_1N_1 + PN_2 + R_2N_2$$



where we have assumed nondegenerate levels with statistical weight factors $g_1 = g_2 = 1$.

Under stationary conditions $\frac{dN_i}{dt} = 0$, we obtain with $N_1 + N_2 = N$:

$$(P + R_1)N_1 = (P + R_2)(N - N_1)$$

$$(P + R_2)N_2 = (P + R_1)(N - N_2)$$

leading to:

$$N_1 = N\frac{P + R_2}{2P + R_1 + R_2} \qquad N_2 = N\frac{P + R_1}{2P + R_1 + R_2}$$

2.3 SATURATION AND POWER BROADENING

When the pump rate P becomes much larger than the relaxation rates R_i $(P \gg R_1, R_2)$, the population $N_1 = N_2 \approx \frac{N}{2}$ and so $N_1 = N_2$.

$$N_1 = N \frac{P + R_2}{2P + R_1 + R_2}$$

$$N_2 = N \frac{P + R_1}{2P + R_1 + R_2}$$

This means that the absorption coefficient $\alpha = \sigma(N_1 - N_2) = 0$.

The medium becomes completely transparent..

Without a radiation field $(P = 0)$, the population densities at thermal equilibrium according are (using previous expressions):

$$N_{10} = N \frac{R_2}{R_1 + R_2} \qquad N_{20} = N \frac{R_1}{R_1 + R_2}$$

With the abbreviations

$$\Delta N = N_1 - N_2 = N \frac{R_2 - R_1}{2P + R_1 + R_2}$$

$$\Delta N_0 = N_{10} - N_{20} = N \frac{R_2 - R_1}{R_1 + R_2}$$

2.3 SATURATION AND POWER BROADENING

Dividing both members of ΔN with $R_1 + R_2$ we obtain:

$$\Delta N = \frac{\Delta N_0}{1 + \frac{2P}{R_1 + R_2}}$$

$$\Delta N = N_1 - N_2 = N\frac{R_2 - R_1}{2P + R_1 + R_2}$$

$$\Delta N_0 = N_{10} - N_{20} = N\frac{R_2 - R_1}{R_1 + R_2}$$

We introduce the **saturation parameter**:

$$S = \frac{2P}{R_1 + R_2} = \frac{P}{\overline{R}} = \frac{B_{12}\rho(\omega)}{\overline{R}}$$

where $\overline{R} = \frac{R_1+R_2}{2}$ is the average relaxation rate.

Then the saturation parameter is the ratio between pumping rate and the average relaxation rate of the two levels.

Then, ΔN can be rewritten as: $$\Delta N = \frac{\Delta N_0}{1 + S}$$

and the saturated absorption coefficient $\alpha(\omega) = \sigma_{12}\Delta N$ becomes:

$$\alpha = \frac{\alpha_0}{1 + S}$$

where α_0 is the unsaturated absorption coefficient without pumping.

2.3 SATURATION AND POWER BROADENING

The power absorbed per unit volume on the transition $|1\rangle \rightarrow |2\rangle$ by atoms with the population densities $N_1$and N_2 in a radiation field with a broad spectral profile and spectral energy density $\rho(\omega)$ will be:

$$\frac{dW_{12}}{dt} = \hbar\omega B_{12}\rho(\omega)\Delta N$$

Replacing $\Delta N = \frac{\Delta N_0}{1+S}$, you get:

$$\frac{dW_{12}}{dt} = \hbar\omega B_{12}\rho(\omega)\frac{\Delta N_0}{1+S}$$

With $S = \frac{B_{12}\rho(\omega)}{\overline{R}}$, from which $B_{12}\rho(\omega) = S\overline{R}$, you get:

$$\frac{dW_{12}}{dt} = \hbar\omega\overline{R}\frac{\Delta N_0}{1+\frac{1}{S}}$$

2.3 SATURATION AND POWER BROADENING

Since the absorption profile $\alpha(\omega)$ of a homogeneously broadened line is Lorentzian, the induced absorption probability of a monochromatic wave with frequency ω follows a Lorentzian line profile $B_{12}\rho(\omega)L(\omega-\omega_0)$.

We can therefore introduce a frequency-dependent spectral saturation parameter S_ω for the transition $E_1 \rightarrow E_2$:

$$S_\omega = \frac{B_{12}\rho(\omega)}{\overline{R}} L(\omega-\omega_0)$$

$$S = \frac{B_{12}\rho(\omega)}{\overline{R}}$$

We can assume that the mean relaxation rate $\overline{R}$ is independent of ω within the frequency range of the line profile. With the definition of the Lorentzian profile $L(\omega-\omega_0)$, we obtain for the spectral saturation parameter S_ω:

$$S_\omega = S_0 \frac{\left(\frac{\gamma}{2}\right)^2}{(\omega-\omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$

$$L(\omega-\omega_0) = \frac{\left(\frac{\gamma}{2}\right)^2}{(\omega-\omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$

with $S_0 = S_\omega(\omega_0)$

2.3 SATURATION AND POWER BROADENING

$$S_\omega = S_0 \frac{\left(\frac{\gamma}{2}\right)^2}{(\omega-\omega_0)^2+\left(\frac{\gamma}{2}\right)^2}$$

Substituting this expression in $\frac{dW_{12}}{dt} = \hbar\omega\overline{R}\frac{\Delta N_0}{1+\frac{1}{S}}$:

$$\frac{dW_{12}}{dt} = \frac{\hbar\omega\overline{R}\Delta N_0 S_0\left(\frac{\gamma}{2}\right)^2}{(\omega-\omega_0)^2+\left(\frac{\gamma}{2}\right)^2(1+S_0)} = \frac{C}{(\omega-\omega_0)^2+\left(\frac{\gamma_s}{2}\right)^2}$$

This a Lorentzian profile with the increased halfwidth:

$$\gamma_s = \gamma\sqrt{1+S_0}$$

The halfwidth γ_s of the saturation-broadened line increases with the saturation parameter S_0 at the line center ω_0. If the induced transition rate at ω_0 equals the total relaxation rate $\overline{R}$, the saturation parameter $S_0 = \frac{B_{12}\rho(\omega_0)}{\overline{R}}$ becomes equal to 1, which increases the linewidth by a factor $\sqrt{2}$ compared to the unsaturated linewidth for weak radiation fields.

2.3 SATURATION AND POWER BROADENING

Since the power $\frac{dW_{12}}{dt}$ absorbed per unit volume equals the intensity decrease per centimeter

$$dI = -\alpha_s I$$

of an incident wave with intensity I, we can derive the expression for the absorption coefficient:

$$\alpha_s(\omega) = \frac{\alpha_0(\omega)}{1 + S_\omega} = \alpha_0(\omega_0) \frac{\left(\frac{\gamma}{2}\right)^2}{(\omega - \omega_0)^2 + \left(\frac{\gamma_s}{2}\right)^2}$$

where the unsaturated absorption profile is:

$$\alpha_0(\omega) = \alpha_0(\omega_0) \frac{\left(\frac{\gamma}{2}\right)^2}{(\omega - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$

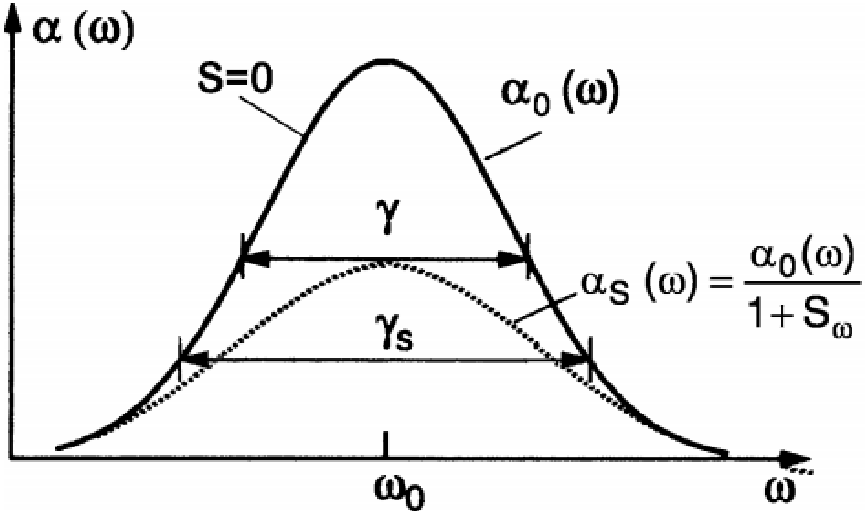
2.3 SATURATION AND POWER BROADENING

This shows that the saturation decreases the absorption coefficient $\alpha(\omega)$ by a factor of $1 + S_\omega$.

At the line center, this factor has its maximum value $1 + S_0$, while it decreases for increasing $(\omega - \omega_0)$: The saturation is therefore strongest at the line center, and approaches zero for $(\omega - \omega_0) \rightarrow \infty$.

This is the reason why the line broadens.

$$\alpha_s(\omega) = \frac{\alpha_0(\omega)}{1 + S_\omega}$$



EXERCISE 1

EXERCISE 1

Determine the natural linewidth, the Doppler width, pressure broadening and shifts for the neon transition $3s_2 \rightarrow 2p_4$ a $\lambda = 632.8\,nm$ in a HeNe discharge at $p_{He} = 2\,mbar$, $p_{Ne} = 0.2\,mbar$ at a gas temperature of $400\,K$. The relevant data are: $\tau(3s_2) = 58\,ns$, $\tau(2p_4) = 18\,ns$, $\sigma_B(Ne - He) = 6 \cdot 10^{-14} cm^2$ e $\sigma_B(Ne - Ne) = 1 \cdot 10^{-13} cm^2$.

Considering the lifetimes of the two levels $3s_2$ e $2p_4$, the natural linewidth is:

$$\delta\nu_n = \frac{\sum_i A_i}{2\pi} = \frac{1}{2\pi}\sum_i \frac{1}{\tau_i} = \frac{1}{2\pi}\left(\frac{1}{\tau(3s_2)} + \frac{1}{\tau(2p_4)}\right)$$

$$= \frac{1}{2\pi}(1.72 \cdot 10^7 s^{-1} + 1.56 \cdot 10^7 s^{-1}) = 1.16 \cdot 10^7 s^{-1} = 11.6\,MHz$$

EXERCISE 1

The Doppler width is given by:

$$\delta\omega_D = \left(\frac{\omega_0}{c}\right)\sqrt{\frac{8kTln2}{m}}$$

This expression can be rewritten in a more convenient way in terms of the Avogadro number N_A (number of molecules per mole). The mass of a mole is $M = N_A m$ and the gas constant is $R = N_A k$. Using these relations, the Doppler width becomes:

$$\delta\omega_D = 2\left(\frac{\omega_0}{c}\right)\sqrt{\frac{2RTln2}{M}}$$

Being: $R = 8.31\,\frac{J}{mol\cdot K}$

you get:

$$\delta\upsilon_D = 7.16\cdot 10^{-7}\upsilon_0\sqrt{\frac{T}{M}}$$

EXERCISE 1

$$\delta \upsilon_D = 7.16 \cdot 10^{-7} \upsilon_0 \sqrt{\frac{T}{M}}$$

In our case:

$$\upsilon_0 = \frac{c}{\lambda} = 4.74 \cdot 10^{14} Hz$$

$$M = M_{Ne} = 20u$$

with $u = 1.66 \cdot 10^{-27}$ kg unified atomic mass unit

Substituting the values:

$$\delta \upsilon_D = 7.16 \cdot 10^{-7} \cdot 4.74 \cdot 10^{14} Hz \sqrt{\frac{400\ K}{20}} = 1.52\ GHz$$

EXERCISE 1

For broadening due to collisions, let us consider two contributions:

1. Collisions with He atoms

$$\delta\upsilon_{P,He} = \frac{1}{2\pi} n_{He}\sigma_B(Ne - He)\bar{v}$$

At $p_{He} = 2\ mbar$ and $\mathrm{T} = 400\ K$, using the ideal gas law:

$$n_{He} = \frac{p}{kT} = \frac{200\ Pa}{1.38\cdot 10^{-23}\frac{J}{K}\cdot 400\ K} = 3.6\cdot 10^{16}cm^{-3}$$

Let's determine the mean velocity. Being $\mu = \frac{M_{He}M_{Ne}}{M_{Ne}+M_{Ne}} = 3.3u$

$$\bar{v} = \sqrt{\frac{8KT}{\pi\mu}} = \sqrt{\frac{8\cdot 1.38\cdot 10^{-23}\frac{J}{K}\cdot 400\ K}{3.14\cdot 3.3\cdot 1{,}66\cdot 10^{-27}\ \mathrm{kg}}} = 1.59\cdot 10^{5}cm/s$$

EXERCISE 1

Then the line broadening due to collisions with He atoms:

$$\delta\upsilon_{P,He} = \frac{1}{2\pi} n_{He}\sigma_B(Ne-He)\bar{v} = \frac{3.6\cdot 10^{16}cm^{-3}\cdot 6\cdot 10^{-14}cm^2\cdot 1.59\cdot 10^5 cm/s}{2\cdot 3.14} = 55\ MHz$$

2. Collisions with Ne atoms

$$\delta\upsilon_{P,Ne} = \frac{1}{2\pi} n_{Ne}\sigma_B(Ne-Ne)\bar{v}$$

At $p_{He} = 0.2\ mbar$ and $\mathrm{T} = 400\ K$, using the ideal gas law:

$$n_{Ne} = \frac{p}{kT} = \frac{20\ Pa}{1.38\cdot 10^{-23}\frac{J}{K}\cdot 400\ K} = 3.6\cdot 10^{15}cm^{-3}$$

The mean velocity: ($\mu = \frac{M_{Ne}M_{Ne}}{M_{Ne}+M_{Ne}} = \frac{1}{2}M_{Ne} = 10u$)

$$\bar{v} = \sqrt{\frac{8KT}{\pi\mu}} = \sqrt{\frac{8\cdot 1.38\cdot 10^{-23}\frac{J}{K}\cdot 400\ K}{3.14\cdot 10\cdot 1{,}66\cdot 10^{-27}\ \mathrm{kg}}} = 9{,}2\cdot 10^4 cm/s$$

EXERCISE 1

Then the line broadening due to collisions with Ne atoms:

$$\delta\upsilon_{P,Ne} = \frac{1}{2\pi} n_{Ne}\sigma_B(Ne - Ne)\bar{v} = \frac{3.6 \cdot 10^{15} cm^{-3} \cdot 1 \cdot 10^{-13} cm^2 \cdot 9.2 \cdot 10^4 cm/s}{2 \cdot 3.14} = 5\, MHz$$

The total contribution to the line broadening due to collisions will be:

$$\delta\upsilon_P = \delta\upsilon_{P,He} + \delta\upsilon_{P,Ne} = 55\, MHz + 5\, MHz = 60\, MHz$$

In summary, the different contributions to the line broadening of the transition will be:

Natural linewidth	11.6 MHz
Doppler width	1.52 GHz
Collisional broadening	60 MHz

Even though gas is at very low pressures (< 0.2% of atmospheric pressure), Doppler broadening overcome all other contributions!

EXERCISE 2

EXERCISE 2

The output from a CO_2 laser with $50\,W$ at $\lambda = 10\,\mu m$ is focussed into a sample of SF_6 molecules at the pressure $p = 1\,mbar$ and $\mathrm{T} = 300\,K$. The laser beam waist in the focal plane is $0.5\,mm$. Being the broadening cross section $\sigma_B = 5 \cdot 10^{-14} cm^2$ and the absorption cross section $\sigma_a = 10^{-14}\,cm^2$, determine which is the dominant broadening mechanism for the absorption line.

Let's neglect the natural linewidth. The pressure broadening will be:

$$\delta v_p = \frac{1}{2\pi} n_{SF6} \sigma_B \bar{v}$$

At $p_{SF6} = 1\,mbar$ and $\mathrm{T} = 300\,K$, using the ideal gas law:

$$n_{SF6} = \frac{p}{kT} = \frac{100\,Pa}{1.38 \cdot 10^{-23} \frac{J}{K} \cdot 300\,K} = 2.4 \cdot 10^{22}\,m^{-3}$$

EXERCISE 2

The average velocity will be ($M_{SF6} = 146u$)

$$\bar{v} = \sqrt{\frac{8KT}{\pi M_{SF6}}} = \sqrt{\frac{8 \cdot 1.38 \cdot 10^{-23} \frac{J}{K} \cdot 400\ K}{3.14 \cdot 146 \cdot 1{,}66 \cdot 10^{-27}\ \text{kg}}} = 209\ m/s$$

So, the collisional broadening will be:

$$\delta v_P = \frac{1}{2\pi} n_{SF6} \sigma_B \bar{v} = \frac{2.4 \cdot 10^{22} m^{-3} \cdot 5 \cdot 10^{-18} m^2 \cdot 209\ m/s}{2 \cdot 3.14} = 4\ MHz$$

The saturation broadening δv_s caused by the absorption of laser light, in terms of the saturation parameter S, is:

$$\delta v_s = \delta v_p \sqrt{1+S}$$

The saturation parameter is defined as the ratio of the pumping rate to the average relaxation rate .

The pumping rate P can be expressed as:

$$P = \frac{I \sigma_a}{h v}$$

EXERCISE 2

where the intensity of the light can be expressed as the ratio between the power and the irradiated surface A; the latter is the area of the focused laser spot $A = \pi r^2$:

$$I = \frac{P_L}{\pi r^2} = \frac{50\ W}{3.14 \cdot 0.5^2 \cdot 10^{-2} cm^2} = 6.4 \cdot 10^3 \frac{W}{cm^2}$$

Neglecting the natural linewidth, the average relaxation rate is:

$$\gamma = 2\pi\delta\upsilon_P$$

and then the saturation parameter can be expressed as:

$$S = \frac{P}{\gamma} = \frac{I\sigma_a}{2\pi\delta\upsilon_P\, h\upsilon} = \frac{I\sigma_a\lambda}{2\pi\delta\upsilon_P\, hc}$$

$$= \frac{6.4 \cdot 10^3 \frac{W}{cm^2} \cdot 10^{-14}\ cm^2 \cdot 10 \cdot 10^{-4} cm}{6.28 \cdot 4 \cdot 10^6 Hz \cdot 6.63 \cdot 10^{-34} Js \cdot 3 \cdot 10^{10} cm/s} = 128$$

The saturation broadening will be:

$$\delta\upsilon_s = \delta\upsilon_p \sqrt{1+S} = 4\ MHz\sqrt{129} = 44\ MHz$$

EXERCISE 2

Finally, the Doppler width is:

$$\delta \upsilon_D = 7.16 \cdot 10^{-7} \frac{c}{\lambda} \sqrt{\frac{T}{M_{SF6}}} = 7.16 \cdot 10^{-7} \cdot \frac{3 \cdot 10^{10} \frac{cm}{s}}{10 \cdot 10^{-4} cm} \cdot \sqrt{\frac{300}{146}} = 30.8\, MHz$$

In summary, the different contributions to the line broadening of the transition will be:

Collisional broadening	4 MHz
Doppler width	30.8 MHz
Saturation broadening	44 MHz

Saturation broadening is the dominant mechanism.