

$$n_i'(\omega) = 1 + \frac{N_i e^2}{2m\epsilon_0} \sum_k \frac{(\omega_{ik}^2 - \omega^2) f_{ik}}{(\omega_{ik}^2 - \omega^2)^2 + \gamma_{ik}^2 \omega^2} \quad (366)$$

$$K_i(\omega) = \frac{N_i e^2}{2m\epsilon_0} \sum_k \frac{\gamma_{ik} \omega f_{ik}}{(\omega_{ik}^2 - \omega^2)^2 + \gamma_{ik}^2 \omega^2} \quad (367)$$

These are the QM-corrected complex refractive index

$$n_i(\omega) = n_i'(\omega) - i K_i(\omega) \quad (368)$$

Example: The f value of the Na D-lines is

$$f(3S - 3^2P_{1/2}) = 0.320, \quad f(3S - 3^2P_{3/2}) = 0.641$$

This implies that the two D-lines carry 96% of the total oscillator strength out of the ground state 3S.

(3) Absorption and Dispersion

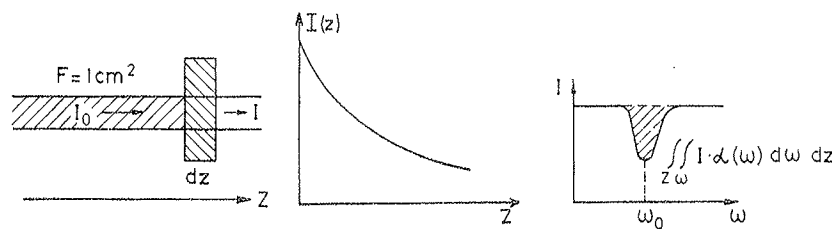


Fig. Absorption of light in an optically thin layer

Generally the absorption of radiation passing through a medium is characterized by the absorption coefficient α which describes the attenuation of the radiation intensity (rather than the amplitude). If the intensity of a plane wave is $I(z)$, its attenuation along the distance dz is

$$dI = -\alpha I dz \quad (369)$$

The absorption coefficient α represents the fraction dI/I absorbed

Within the unit interval $dz = 1 \text{ cm}$. For constant α (ie., independent of I), integration of Eq.(369) yields Beer's law for linear absorption ($dI \propto I$):

$$I(z) = I_0 e^{-\alpha z} \quad (370)$$

where I_0 is the intensity at $z=0$.

Using Eq.(361) and considering $I \propto E \cdot E^*$

$$\therefore I(z) = I_0 e^{-2k_0 k(\omega)z} \quad (371).$$

Compare Eq.(371) with Eq.(370), we obtain the absorption coefficient

$$\alpha = 2k_0 k(\omega) = 4\pi k(\omega)/\lambda_0 \quad (372)$$

Thus, the absorption coefficient is proportional to the imaginary part of the complex refraction index $n = n' - ik$.

Using the classical model $n(\omega)$ given by Eqs.(362) and (363),

We have

$$\left\{ \begin{aligned} \alpha(\omega) &= 4\pi k_i(\omega)/\lambda_0 = \frac{2\omega_0 k(\omega)}{c} \\ &= \frac{Nq^2\omega_0}{cm\epsilon_0} \cdot \frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \quad (373) \\ n'(\omega) &= 1 + \frac{Nq^2}{2m\epsilon_0} \cdot \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \quad (374) \end{aligned} \right.$$

For $|\omega_0 - \omega| \ll \omega_0$, $\omega_0 + \omega \approx 2\omega$. Thus, Eqs.(373) and (374)

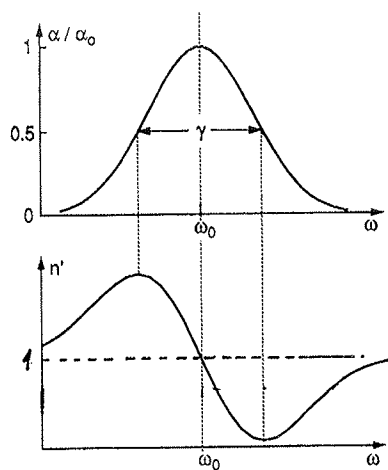
can be simplified with $q = -e$ to

$$\left\{ \begin{aligned} \alpha(\omega) &= \frac{Ne^2}{4m\epsilon_0 c} \cdot \frac{\gamma}{(\omega_0 - \omega)^2 + (\gamma/2)^2} \quad (375) \end{aligned} \right.$$

$$\left\{ \begin{aligned} n'(\omega) &= 1 + \frac{Ne^2}{4m\epsilon_0 \omega_0} \cdot \frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + (\gamma/2)^2} \quad (376) \end{aligned} \right.$$

Eqs. (375) and (376) give the Kramers-Kronig Dispersion Relations.

Here, m is the mass of electrons. The dispersion relation is shown in the figure below.



Absorption $\alpha(\omega)$ — Lorentzian shape
with $\text{FWHM} = \Delta\omega_n = \gamma$

Dispersion $n'(\omega)$ — dispersion profile
 $n'(\omega = \omega_0) = 1$.

Fig. 3.5. Absorption coefficient $\alpha = 2k\kappa(\omega)$ and dispersion $n'(\omega)$ in the vicinity of an atomic transition with center frequency ω_0

Using the QM-corrected refraction index $n(\omega)$ given by Eq. (366) and Eq. (367), we have

$$\left\{ \begin{aligned} \alpha_i(\omega) &= \frac{N_i e^2}{m \epsilon_0 c} \sum_k \frac{\gamma_{ik} \omega \omega_{ik} f_{ik}}{(\omega_{ik}^2 - \omega^2)^2 + \gamma_{ik}^2 \omega^2} \end{aligned} \right. \quad (377)$$

$$\left\{ \begin{aligned} n'_i(\omega) &= 1 + \frac{N_i e^2}{2m \epsilon_0} \sum_k \frac{(\omega_{ik}^2 - \omega^2) f_{ik}}{(\omega_{ik}^2 - \omega^2)^2 + \gamma_{ik}^2 \omega^2} \end{aligned} \right. \quad (378)$$

For $|\omega_{ik} - \omega| \ll \omega_{ik}$, $\omega_{ik} + \omega \approx 2\omega$, then Eqs. (377-378) can be

Simplified to

$$\left\{ \begin{aligned} \alpha_i(\omega) &= \frac{N_i e^2}{4m \epsilon_0 c} \sum_k \frac{\gamma_{ik} f_{ik}}{(\omega_{ik} - \omega)^2 + (\gamma_{ik}/2)^2} \end{aligned} \right. \quad (379)$$

$$\left\{ \begin{aligned} n'_i(\omega) &= 1 + \frac{N_i e^2}{4m \epsilon_0} \sum_k \frac{[(\omega_{ik} - \omega)/\omega_{ik}] f_{ik}}{(\omega_{ik} - \omega)^2 + (\gamma_{ik}/2)^2} \end{aligned} \right. \quad (380)$$

This is for the case when the radiation field has wide spectrum to cover many transition lines. $|i\rangle \rightarrow |k\rangle$.

However, in spectroscopy, we have the case that the radiation field has narrow spectrum, and only excites one transition.

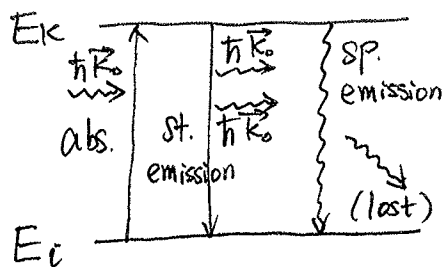
If we write $\omega_0 = \omega_{ik}$ for this transition, then

$$\alpha_{ik}(\omega) = \frac{N_i e^2}{4m\epsilon_0 c} \cdot \frac{\gamma_{ik} f_{ik}}{(\omega_0 - \omega)^2 + (\gamma_{ik}/2)^2} \quad (381)$$

$$n'_{ik}(\omega) = 1 + \frac{N_i e^2}{4m\epsilon_0 \omega_0} \cdot \frac{(\omega_0 - \omega) f_{ik}}{(\omega_0 - \omega)^2 + (\gamma_{ik}/2)^2} \quad (382)$$

Compared to the classical model results Eq.(375) and Eq.(376), the QM results Eqs.(381) and (382) have the extra factor — the oscillator strength.

The absorption coefficient can be derived from another point-of-view. The absorption coefficient α_{ik} for a transition $|i\rangle \rightarrow |k\rangle$ depends on the population densities N_i and N_k of the lower and upper levels, and on the optical absorption cross-section σ_{ik} of each atom. Note: α_{ik} has unit of cm^{-1} , while σ_{ik} has unit of cm^2 .



Keep in mind that the stimulated emitted photons travel in the same direction as the incident photons, while the spontaneously emitted photons go any directions.

Thus, spontaneous emission counts for the attenuation of radiation intensity, while stimulated emission does not attenuate the radiation intensity.

$$\therefore \alpha_{ik}(\omega) = N_i \sigma_{ik} - N_k \sigma_{ki} \quad (383)$$

$$\because g_i \sigma_{ik} = g_k \sigma_{ki}, \quad \therefore \sigma_{ki} = \frac{g_i}{g_k} \sigma_{ik}$$

Thus, the absorption coefficient becomes

$$\alpha_{ik}(\omega) = \sigma_{ik}(\omega) \left[N_i - \frac{g_i}{g_k} N_k \right] \quad (384)$$

Usually, E_k is well above E_i . Under weak radiation field, we have

$$N_k \ll N_i$$

Thus, the 2nd term in Eq.(384) can be neglected. Therefore,

$$\alpha_{ik}(\omega) \approx \sigma_{ik}(\omega) N_i \quad (385)$$

Compared with Eq.(379), we obtain the absorption cross-section (with the frequency interval):

$$\sigma_{ik}(\omega) = \frac{e^2}{4m\epsilon_0 c} \sum_k \frac{\gamma_{ik} f_{ik}}{(\omega_{ik} - \omega)^2 + (\gamma_{ik}/2)^2} \quad (386)$$

If there is only one transition being excited by the radiation field, then we have the absorption cross-section

$$\sigma_{ik}(\omega) = \frac{e^2 f_{ik}}{4m\epsilon_0 c} \cdot \frac{\gamma_{ik}}{(\omega_0 - \omega)^2 + (\gamma_{ik}/2)^2} \quad (387)$$

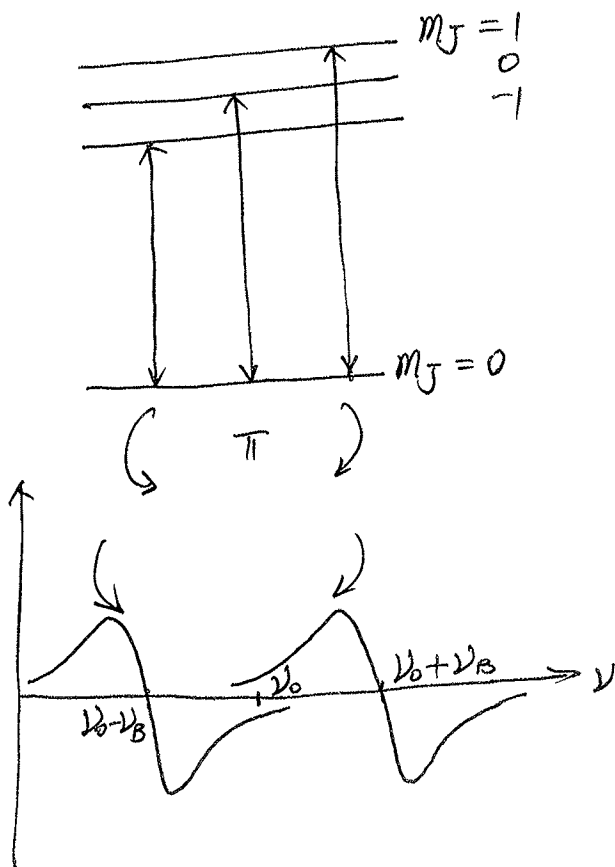
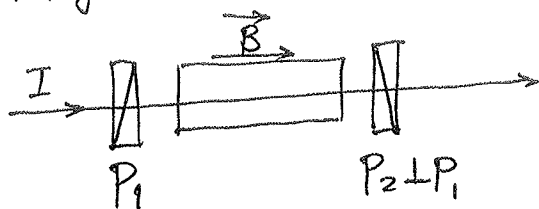
At peak frequency $\omega = \omega_0 (= \omega_{ik})$,

$$\sigma_{ik}(\omega = \omega_0) = \frac{e^2 f_{ik}}{\gamma_{ik} m \epsilon_0 c} \quad (388)$$

Eqs.(386)-(388) are the absorption cross section $\sigma_{ik}(\omega)$ under the Lorentzian line profile.

Example for Dispersion:

Magnetic rotation of polarization \rightarrow resonant Faraday effect.



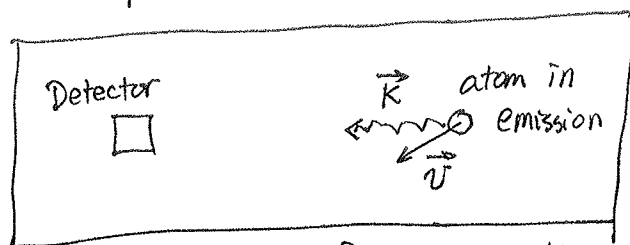
- Linear polarization \rightarrow decomposed into two circular polarization
- \rightarrow experience difference refraction index due to dispersion
 - and Zeeman splitting of magnetic energy level
 - $\rightarrow \Delta n$ causes phase shift between two circular polarizations
 - \rightarrow rotation of linear polarization when recombine.

§7.4. Doppler Linewidth and Lineshape

Generally the Lorentzian line profile with the natural linewidth $\delta\nu_n$, as discussed in the previous section, 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.

Doppler effect is the phenomenon of frequency or wavelength shift when radiation source and receiver have relative motion. It was first described by Doppler. A typical example is the blown whistle of an approaching train: people feel the sound is "sharper" than it's at rest; while the whistle from a train leaving us sounds lower frequency than it's at rest. This means that when the radiation source (e.g., the train) moves towards the receiver (e.g., human's ears), the radiation (e.g., sound wave) frequency increases (i.e., wavelength becomes shorter — blue shift); when the radiation source moves away from the receiver, the radiation frequency decreases (i.e., wavelength becomes longer — red shift). The key point here is the relative motion between the emitter of the radiation (i.e., the source) and the receiver.

Consider an excited molecules with a velocity \vec{v} relative to the rest frame of the observer. In the rest frame, an atom at rest emits a photon with frequency ω_0 .



Doppler shift for emission line

When the atom moves relative to the detector with velocity \vec{v} , the frequency received by the detector becomes:

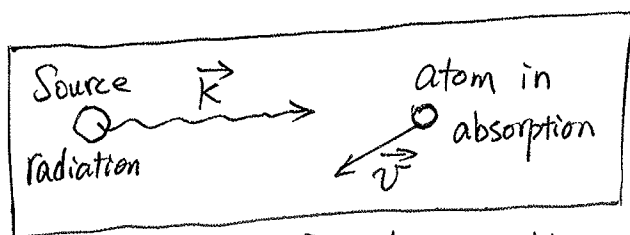
$$\omega_e = \omega_0 + \vec{k} \cdot \vec{v} \quad (389)$$

When the atom moves towards the detector, $\vec{k} \cdot \vec{v} > 0$

$$\therefore \omega_e > \omega_0 \quad (\text{blue shift}) \quad (390)$$

When the atom moves away from the detector, $\vec{k} \cdot \vec{v} < 0$

$$\therefore \omega_e < \omega_0 \quad (\text{red shift}) \quad (391)$$



Doppler Shift for absorption line

At rest, the resonance frequency for the atomic absorption is ω_0 .

If the atom moves relative to the detector with velocity \vec{v} , the

apparent frequency of the radiation changes from its at rest frequency ω to a shifted frequency ω'

$$\omega' = \omega - \vec{k} \cdot \vec{v} \quad (392)$$

When $\omega' = \omega_0$, the atom will have resonance absorption.

Thus, the absorption frequency $\omega = \omega_a$ is given by

$$\omega_a = \omega_0 + \vec{k} \cdot \vec{v} \quad (393)$$

Eqs. (389) and (393) are the expression of Doppler Shift in vector.

The shift of absorption frequency is actually opposite to emission freq.

When the atom moves towards the radiation source, $\vec{k} \cdot \vec{v} < 0$

$$\therefore \omega_a < \omega_0 \quad (\text{red shift})$$

When the atom moves away from the radiation source, $\vec{k} \cdot \vec{v} > 0$

$$\therefore \omega_a > \omega_0 \quad (\text{blue shift})$$

But when expressed in vector, they have the same equation:

$$\omega_{e/a} = \omega_0 \pm \vec{k} \cdot \vec{v} \quad (394)$$

If expressed in scalar, i.e., write out $\vec{k} \cdot \vec{v} = kv \cos \theta$, where θ is the angle between \vec{k} and \vec{v} . Then the sign (+ or -) will

depend on $\cos \theta$. Usually, we define one direction as positive,

e.g., when measuring vertical wind by lidar, define upward as $v_z = W > 0$. Laser pulse comes from ground, propagating

upward, so $k_z = \frac{2\pi}{\lambda_0} = \frac{2\pi\nu_0}{c} = \frac{\omega_0}{c} > 0$.

Thus, the absorption frequency of the atom becomes

$$\omega_a = \omega_0 + k_z \cdot v_z = \omega_0 \left(1 + \frac{v_z}{c}\right) \quad (395)$$

When the atom with upward velocity $v_z > 0$ emits a photon, the receiver is at ground, so the photon propagates downward,

$k_z = -\frac{2\pi}{\lambda_0} = -\frac{\omega_0}{c} < 0$. Thus, the emission frequency

$$\omega_e = \omega_0 - \frac{\omega_0}{c} v_z = \omega_0 \left(1 - \frac{v_z}{c}\right) \quad (396)$$

Thus, the frequency shift between ω_a and ω_e is

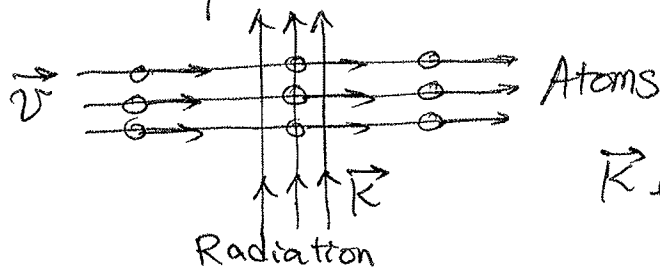
$$\Delta\omega = \omega_a - \omega_e = 2\omega_0 \frac{v_z}{c} \quad (397)$$

Above we discussed the linear Doppler shift $\vec{k} \cdot \vec{v} = kv \cos \theta$.

Apparently, if $\theta = 90^\circ$, i.e., $\vec{k} \perp \vec{v}$, then this shift is zero.

In other words, we can avoid the first order Doppler shift by making the radiation field perpendicular to the velocity of atoms. This is why atomic beam or molecular beam is very

useful:



$$\vec{k} \perp \vec{v} \Rightarrow \vec{k} \cdot \vec{v} = 0$$

Atomic/molecular beam to avoid 1st order Doppler shift.

Besides the 1st order, there are quadratic Doppler shift (2nd order) that is independent of velocity direction, but depends on the absolute value of $|\vec{v}|$. The minimization of 2nd order Doppler shift can only be done by laser cooling to decrease $|\vec{v}|$. This will be discussed in later laser spectroscopy.

For normal situation, atoms or molecules move randomly under thermal equilibrium (no fixed direction like atomic beam). They follow a Maxwellian velocity distribution. At the temperature

T , the number of molecules $n_i(v_z)dv_z$ in the level E_i per unit volume with a velocity component between v_z and $v_z + dv_z$ is

$$n_i(v_z)dv_z = \frac{N_i}{v_p \sqrt{\pi}} e^{-(v_z/v_p)^2} dv_z, \quad (398)$$

where $N_i = \int n_i(v_z)dv_z$ is the total population density on level

E_i , $v_p = \sqrt{2k_B T/m}$ is the most probable velocity, m is the mass

of a molecule, and k_B is Boltzmann's constant.

$$\text{From Eq. (395), } \nu_z = \frac{c(\omega - \omega_0)}{\omega_0}, \quad d\nu_z = \frac{c}{\omega_0} d\omega. \quad (399)$$

Inserting Eq. (399) into Eq. (398) gives the number of molecules with absorption frequencies shifted from ω_0 into the interval from ω to $\omega + d\omega$:

$$n_i(\omega) d\omega = N_i \frac{c}{\omega_0 \nu_p \sqrt{\pi}} e^{-\left[\frac{c(\omega - \omega_0)}{\omega_0 \nu_p}\right]^2} d\omega \quad (400)$$

Substitute ν_p equation into Eq. (400) and recall $\omega_0 = \frac{2\pi c}{\lambda_0}$, we get

$$n_i(\omega) d\omega = N_i \frac{1}{2\pi \sqrt{2\pi} \sqrt{\frac{k_B T}{m \lambda_0^2}}} \exp\left[-\frac{(\omega - \omega_0)^2}{(2\pi)^2 2 \cdot \frac{k_B T}{m \lambda_0^2}}\right] d\omega$$

Define the rms width for this Gaussian shape as

$$\sigma_D = \sqrt{\frac{k_B T}{m \lambda_0^2}} \quad (401)$$

$$\therefore n_i(\omega) d\omega = \frac{N_i}{2\pi \cdot \sqrt{2\pi} \sigma_D} \exp\left[-\frac{(\omega - \omega_0)^2}{(2\pi)^2 2 \sigma_D^2}\right] d\omega \quad (402)$$

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

$$I(\omega) = I_0 \exp\left[-\frac{(\omega - \omega_0)^2}{(2\pi)^2 2 \sigma_D^2}\right] \quad (403)$$

This is a Gaussian profile with a full width at half maximum (FWHM)

$$\delta\omega_D = \sqrt{8 \ln 2} \cdot 2\pi \cdot \sigma_D = 2\pi \sqrt{\frac{8 \ln 2 \cdot k_B T}{m \lambda_0^2}} \quad (404)$$

Using $\delta\omega_D$, Eq. (403) becomes

$$I(\omega) = I_0 \exp\left[-\frac{(\omega - \omega_0)^2}{(\delta\omega_D)^2 / (4 \ln 2)}\right] = I_0 \exp\left[-\frac{(\omega - \omega_0)^2}{0.36(\delta\omega_D)^2}\right] \quad (405)$$

Below is a comparison of Lorentzian and Gaussian line profiles with equal FWHM.

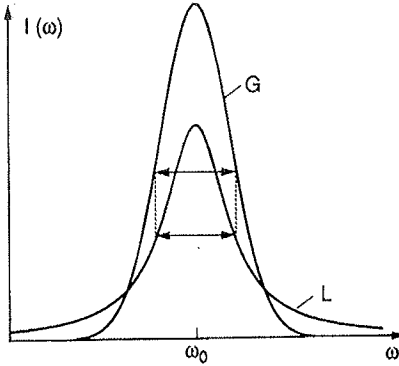


Fig. 3.7. Comparison between Lorentzian (L) and Gaussian (G) line profiles of equal halfwidths

The intensity I approaches zero for large arguments $(\nu - \nu_0)$ much faster for a Gaussian line profile than for a Lorentzian profile.

Define the normalized Gaussian line profile as

$$g_D(\omega) = \frac{1}{\sqrt{2\pi} (2\pi\sigma_D)} \exp\left[-\frac{(\omega - \omega_0)^2}{2(2\pi\sigma_D)^2}\right] \quad (406)$$

$$\therefore \int_0^{\infty} g_D(\omega) d\omega = \int_{-\infty}^{+\infty} g_D(\omega - \omega_0) d(\omega - \omega_0) = 1. \quad (407)$$

$$\therefore I(\omega) = I_0 \cdot \sqrt{2\pi} \cdot (2\pi\sigma_D) \cdot g_D(\omega) \quad (408)$$

$$\text{Total Energy } I_T = \int I(\omega) d\omega = I_0 (2\pi\sigma_D) \sqrt{2\pi} \int g_D(\omega) d\omega = I_0 (2\pi\sigma_D) \sqrt{2\pi} \quad (409)$$

If we write in ν unit ($\nu = \omega/2\pi$), then

$$g(\nu) = \frac{1}{\sqrt{2\pi} \sigma_D} \exp\left[-\frac{(\nu - \nu_0)^2}{2\sigma_D^2}\right] \quad (410)$$

$$\therefore I(\nu) = I_0' \cdot \sigma_D \cdot \sqrt{2\pi} \cdot g_D(\nu) = I_0' \exp\left[-\frac{(\nu - \nu_0)^2}{2\sigma_D^2}\right] \quad (411)$$

$$\therefore I_T = \int I(\nu) d\nu = I_0' \sigma_D \cdot \sqrt{2\pi} = I_0 (2\pi\sigma_D) \sqrt{2\pi} \quad (412)$$

$$\therefore I_0' = 2\pi I_0 \quad (413)$$

More detailed consideration shows that a Doppler-broadened spectral line cannot be strictly represented by a pure Gaussian profile, because of the natural linewidth caused by finite lifetime.

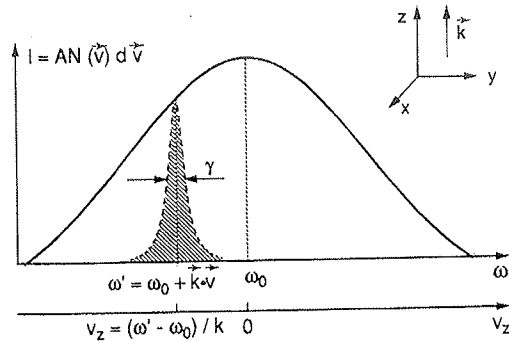


Fig. 3.8. Lorentzian profile centered at $\omega' = \omega_0 + k \cdot v = \omega_0(1 + v_z/c)$ for molecules with a definite velocity component v_z

Natural linewidth has a Lorentzian profile @ each $\omega' = \omega_0 + \vec{k} \cdot \vec{v}$

$$g_L(\omega) = \frac{\gamma/2\pi}{(\omega - \omega')^2 + (\gamma/2)^2} \quad (414)$$

Thus, the spectral intensity distribution $I(\omega)$ of the total absorption or emission of all molecules at the transition $E_i \rightarrow E_k$ is the convolution of the Lorentzian profile with the Gaussian profile:

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

$$= \frac{I_0 (\gamma/2\pi) N_i}{\sqrt{2\pi} (2\pi\sigma_D)} \int_0^{\infty} \frac{\exp\left[-\frac{(\omega' - \omega_0)^2}{2(2\pi\sigma_D)^2}\right]}{(\omega - \omega')^2 + (\gamma/2)^2} d\omega' \quad (415)$$

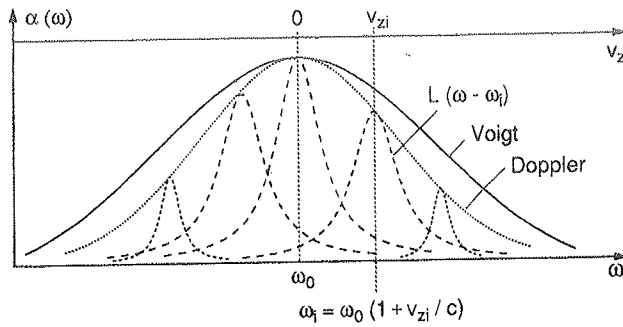


Fig. 3.9. Voigt profile as a convolution of Lorentzian line shapes $L(\omega_0 - \omega_i)$ with $\omega_i = \omega_0(1 + v_{zi}/c)$

This intensity profile, which is a convolution of Lorentzian and Gaussian profiles, is called a Voigt Profile.

§7.5. Transit-Time Broadening

When the interaction time of molecules with the radiation field is small compared with the spontaneous lifetimes of excited levels, the linewidth of a Doppler-free molecular transition is no longer limited by the spontaneous transition probabilities, but by the time of flight through the laser beam, which determines the interaction time of the molecule with the radiation field.

To derive the line profile caused by this transit-time, let us consider an undamped oscillator $x = x_0 \cos \omega_0 t$ that oscillates with constant amplitude x_0 during the time interval T and then suddenly stops oscillating. From Fourier transform,

$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int_0^T x_0 \cos(\omega_0 t) e^{-i\omega t} dt \quad (4.16)$$

The spectral intensity $I(\omega) = A^* A$, for $|\omega - \omega_0| \ll \omega_0$, we obtain

$$I(\omega) = C \frac{\sin^2[(\omega - \omega_0)T/2]}{(\omega - \omega_0)^2} \quad (4.17)$$

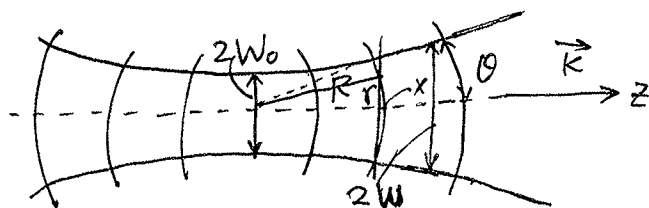
$$\Rightarrow \text{FWHM} : \delta\omega_T = \frac{5.6}{T} \quad (4.18)$$

Full width between the zero points on both sides of ω_0 is

$$\delta\omega_b = \frac{4\pi}{T} \approx \frac{12.6}{T} \quad (4.19)$$

This example is corresponding to an atom that traverses a laser beam with rectangular intensity profile.

In reality, a laser beam usually has a Gaussian beam shape.



$$E = E_0 e^{-r^2/W^2} \cos \omega t \quad (420)$$

where $2W$ gives the diameter of the Gaussian beam profile across the points where $E = E_0/e$.

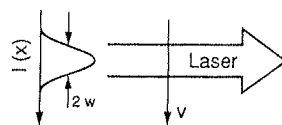
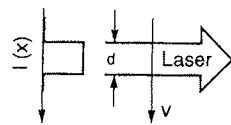
Substitute $X = \alpha E = \alpha E_0 e^{-r^2/W^2} \cos \omega t$ into Eq. (416), we obtain

$$I(\omega) = I_0 \exp \left[-(\omega - \omega_0)^2 \frac{W^2}{2v^2} \right] \quad (421)$$

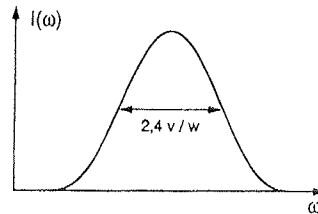
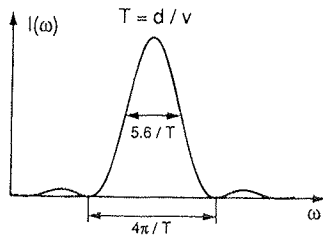
∴ The FWHM for transit time is

$$\delta \omega_{tt} = \frac{v}{W} \sqrt{8 \ln 2} \approx 2.4 v/W \quad (422)$$

$$\therefore \delta \nu_{tt} = \frac{\delta \omega_{tt}}{2\pi} \approx 0.4 v/W \quad (423)$$



(Reducing v to reduce $\delta \nu_{tt}$)
↓
optical cooling



a)

b)

Fig. 3.19a,b. Transition probability $\mathcal{P}(\omega)$ of an atom traversing a laser beam (a) with a rectangular intensity profile $I(x)$; and (b) with a Gaussian intensity profile for the case $v < 1/T = v/d$. The intensity profile $I(\omega)$ of an absorption line is proportional to $\mathcal{P}(\omega)$

Now consider the wave fronts of the focused Gaussian beam are curved except at the focus (waist), an atom moving along the r -direction perpendicular to the laser beam z -axis experiences a spatial phase shift $\Delta \phi = \kappa 2\pi/\lambda$. Thus, the transit-time broadened FWHM

$$\begin{aligned} \text{is: } \delta \omega &= \frac{2v}{W} \sqrt{2 \ln 2} \left[1 + \left(\frac{\pi W^2}{R\lambda} \right)^2 \right] && \text{(Increasing } R \text{ to reduce} \\ &= \delta \omega_{tt} \left[1 + \left(\frac{\pi W^2}{R\lambda} \right)^2 \right] && \text{curvature influence)} \end{aligned} \quad (424)$$

§7.6. Collisional Broadening and Shift of Spectral Lines

Collision-caused spectral line broadening and shift are quite complicated problems. There are mainly two kinds of collisions: inelastic collisions and elastic collisions. They have different effects on line broadening and shift.

(1) Inelastic Collisions — also called quenching collisions

(a) There is internal energy transferred partially or completely from atom A to collision partner B.

Atom A probably gains or loses some kinetic energy to compensate the energy difference between transferred energy and state-change needed energy.

(b) The inelastic collisions force atom A to leave excited state and return to the ground state or transit to another excited state without radiation, i.e., radiationless.

This shortens the lifetime of atom A's excited state,
 \Rightarrow resulting in more uncertainty of the excited level
 \Rightarrow broadening the linewidth of radiation

$$\frac{1}{\tau_k^{\text{eff}}} = \frac{1}{\tau_k} + \frac{1}{\tau_k^{\text{Coll}}} \quad (425)$$

$$A_k^{\text{total}} = A_k^{\text{rad}} + A_k^{\text{Coll}} \quad (426)$$

$$A_k^{\text{total}} = \sum_i' A_{ki} + N_B \sigma_{ik} \bar{v} \quad (427)$$

Where N_B is the number density of the collision partner B, σ_{ik} is the collision cross-section, \bar{v} is the mean relative velocity between A and B.

$$A_k^{\text{Coll}} = N_B \sigma_{ik} \bar{v} \quad (428)$$

From ideal gas law, $P_B = N_B K_B T$ (429)

Where P_B - pressure of B, K_B - Boltzmann Constant, T - temperature.

$$\bar{v} = \sqrt{\frac{8 K_B T}{\pi \mu}} \quad (430)$$

Substitute Eq. (429) and (430) into Eq. (428), We get

$$A_K^{\text{Coll}} = \frac{P_B \sigma_{ik}}{K_B T} \sqrt{\frac{8 K_B T}{\pi \mu}} = P_B \cdot \sigma_{ik} \sqrt{\frac{8}{\pi \mu K_B T}} \quad (431)$$

$$\text{Let } a = \sigma_{ik} \sqrt{\frac{8}{\pi \mu K_B T}} \quad (432)$$

$$\therefore A_K^{\text{Coll}} = a P_B \quad (433)$$

$$\therefore A_K^{\text{total}} = A_K^{\text{rad}} + A_K^{\text{Coll}} = A_K^{\text{rad}} + a P_B = \gamma_n + \gamma_{\text{coll}} \quad (434)$$

Therefore, the spectral linewidth

$$\delta \omega = \delta \omega_n + \delta \omega_{\text{coll}} = \gamma_n + \gamma_{\text{coll}} = \gamma_n + a P_B \quad (435)$$

The inelastic collision-induced additional line broadening

is $\delta \omega_{\text{coll}} = a P_B$, also called pressure broadening.

Since inelastic collision is radiationless, there is no photon emitted during the collision. Therefore, it does not cause frequency shift.

(2). Elastic Collisions: phase-perturbing and velocity-changing collisions

(a) There is no internal energy transfer between atom A and collision partners B, so the collision won't quench A if A is in an excited state for spontaneous emission, but the collision perturbs the phase of A if regarding A as an oscillator.

(b) During collision time, A can undergo a radiative transition.

* The radiation frequency will be determined by the energy difference $\hbar\omega_{ik}(R) = E_k(R) - E_i(R)$ ⁽⁴³⁶⁾ which may be different than ω_0 of the unperturbed atom, i.e., a line shift is resulted. It is mainly due to different shifts of the energy levels E_i and E_k . (If E_i and E_k shift the same amount, then the line shift is zero.)

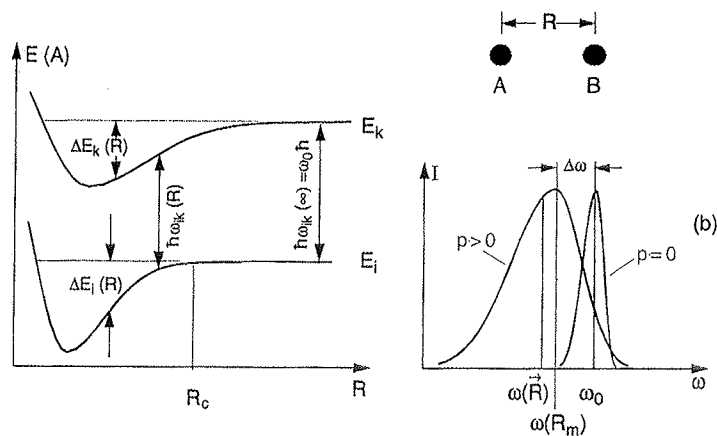


Fig. 3.10. Illustration of collisional line broadening explained with the potential curves of the collision pair AB

Elastic Collision

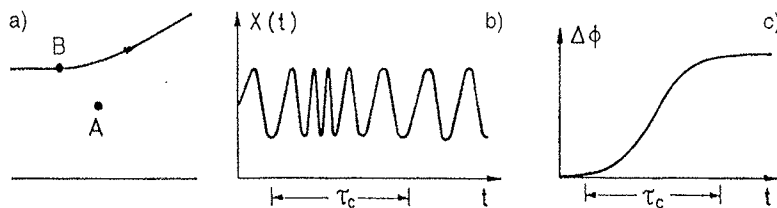


Fig. 3.11a-c. Phase perturbation of an oscillator by collisions: (a) classical path approximation of colliding particles; (b) frequency change of the oscillator $X(t)$ during the collision; (c) resulting phase shift

* The line shifted frequency $\omega_{ik}(R)$ can be different at different collision time or distance R , although it is around a most probable value $\omega_{ki}(R_m)$.

\Rightarrow This will result in a spread of line distribution
 \Rightarrow cause broadening of linewidth.

Therefore, elastic collisions can cause both lineshift and line broadening.

* Lindholm introduced a model to quantitatively describe the line broadening and shift caused by inelastic and elastic collisions. This is to treat the excited atom A as a damped oscillator that suffers collisions with particles B . In this model, inelastic collisions damp the amplitude of the oscillation. This is described by introducing a damp constant γ_{coll} such that the sum of radiative and collisional damping is represented by $\gamma = \gamma_n + \gamma_{coll}$.

Similar to how we derived natural linewidth, the inelastic collision broadened line profile is a Lorentzian:

$$I(\omega) = \frac{C}{(\omega_0 - \omega)^2 + [(\gamma_n + \gamma_{coll})/2]^2} \quad (4.37)$$

$\therefore \delta\omega = \gamma_n + \gamma_{coll}$ under inelastic collision.

The elastic collisions do not change the amplitude, but change the phase of the damped oscillator, due to the frequency shift $\Delta\omega(R)$ during the collisions. Lindholm's results are as follows: line shift of the line center:

$$\Delta\omega = N_B \bar{v} \sigma_s \quad (438)$$

line broadening with Lorentzian shape

$$\delta\omega = 2 N_B \bar{v} \sigma_b \quad (439)$$

\therefore The ~~overall~~ ^{elastic-collision} line profile becomes

$$I(\omega) = I_0 \frac{N_B \bar{v} \sigma_b}{(\omega - \omega_0 - N_B \bar{v} \sigma_s)^2 + (N_B \bar{v} \sigma_b)^2} \quad (440)$$

If we now include additional damping by spontaneous emission and inelastic collisions, we have the overall line profile

$$I(\omega) = I_0 \frac{(\gamma_n/2 + \gamma_{\text{coll}}^{\text{inelastic}}/2 + N_B \bar{v} \sigma_b)^2}{(\omega - \omega_0 - N_B \bar{v} \sigma_s)^2 + [(\gamma_n + \gamma_{\text{coll}}^{\text{inelastic}})/2 + N_B \bar{v} \sigma_b]^2} \quad (441)$$

\therefore Overall linewidth (FWHM)

$$\delta\omega = \gamma_n + \gamma_{\text{coll}}^{\text{inelastic}} + 2 N_B \bar{v} \sigma_b \quad (442)$$

$$= \gamma + 2 N_B \bar{v} \sigma_b$$

($\gamma = \gamma_n + \gamma_{\text{coll}}^{\text{inelastic}}$) (443)

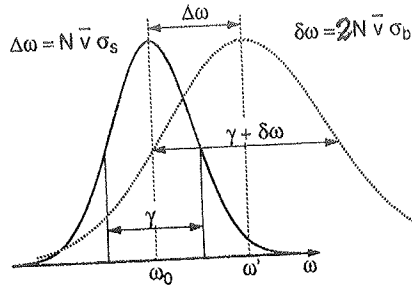


Fig. 3.12. Shift and broadening of a Lorentzian line profile by collisions

$$\therefore N_B = \frac{P_B}{k_B T}, \quad \bar{v} = \sqrt{\frac{8k_B T}{\pi \mu}}, \quad \mu = \frac{M_A M_B}{M_A + M_B}$$

$$\therefore \delta\omega = v_n + a P_B + 2\sigma_b \sqrt{\frac{8}{\pi \mu k_B T}} \cdot P_B$$

$$= v_n + \underbrace{\left(\sigma_{ik} \sqrt{\frac{8}{\pi \mu k_B T}} + 2\sigma_b \sqrt{\frac{8}{\pi \mu k_B T}} \right)}_{\text{collision broadening coefficient}} P_B \quad (444).$$

Line shift:

$$\begin{aligned} \Delta\omega &= N_B \bar{v} \sigma_s \\ &= \underbrace{\sigma_s \sqrt{\frac{8}{\pi \mu k_B T}}}_{\text{collision shift coefficient}} P_B \end{aligned} \quad (445)$$