

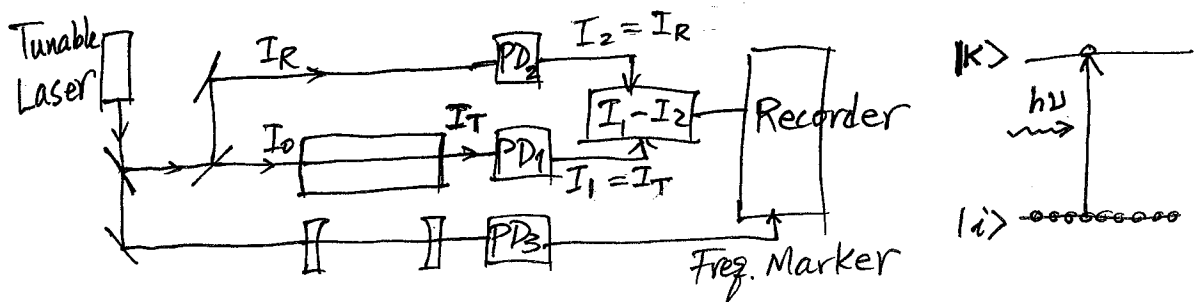
Chapter 14: Doppler-Limited Absorption and Fluorescence Spectroscopy

In this section we mainly concern how to detect atoms and molecules with high sensitivity, based on the absorption of photons by atoms and molecules.

§14.1. General absorption spectra is based on the determination of the absorption coefficient $\alpha(\omega)$ from the transmitted spectral intensity:

$$I_T(\omega) = I_0 e^{-\alpha(\omega)L} \quad (1)$$

where I_0 is the light intensity before entering the sample, $\alpha(\omega)$ is the frequency dependent absorption coefficient, L is the absorption length of the sample, and $I_T(\omega)$ is the transmitted light intensity after the absorption length L .



We split laser into three parts: one for absorption by the sample, one for reference beam of intensity, and the third for going through spectrum analyzer for frequency marker. If the reference beam intensity $I_R = I_0$, i.e.,

$$\left. \begin{aligned} I_2 &= I_R = I_0 \\ \text{and } I_1 &= I_T = I_0 e^{-\alpha(\omega)L} \end{aligned} \right\} (2)$$

Taking the difference between the two channels, we have

$$-\Delta I = I_1 - I_2 = I_T - I_0 = I_0 [e^{-\alpha(\omega)L} - 1] \quad (3)$$

$$\Rightarrow 1 - \frac{\Delta I}{I_0} = e^{-\alpha(\omega)L}$$

$$\Rightarrow \alpha(\omega) = \frac{-\ln(1 - \frac{\Delta I}{I_0})}{L} \quad (4)$$

For small absorption, i.e., $\Delta I \ll I_0$ or $\alpha(\omega) \ll 1$, the above expression can be approximated as

$$\alpha(\omega) = \frac{\Delta I}{I_0 L} = \frac{I_0 - I_T}{I_0 L} \quad (5)$$

(Recall $I_R = I_0$ here).

For transition $|i\rangle \rightarrow |k\rangle$ with absorption cross section σ_{ik} , the absorption coefficient $\alpha_{ik}(\omega)$ is given by

$$\alpha_{ik}(\omega) = [N_i - \frac{g_i}{g_k} N_k] \sigma_{ik}(\omega) = \Delta N \cdot \sigma_{ik}(\omega) \quad (6)$$

$$\therefore \Delta N = \frac{\alpha_{ik}(\omega)}{\sigma_{ik}(\omega)} = \frac{\Delta I}{I_0 L \sigma_{ik}(\omega)} \quad (7)$$

Usually, E_k is much higher than E_i , so the population on $|k\rangle$ state is small enough to be ignored (Boltzmann distribution law),

$$\frac{N_k}{N_i} = \frac{g_k}{g_i} e^{-(E_k - E_i)/k_B T} \quad (8)$$

$N_k \rightarrow 0$ when $E_k \gg E_i$

$$\therefore N_i \approx \Delta N = \frac{\Delta I}{I_0 \cdot L \cdot \sigma_{ik}(\omega)} \quad (9)$$

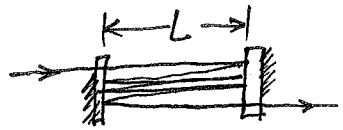
Where $\Delta I = I_0 - I_T$, L is the absorption length.

From Eq. (9), it is obvious that the minimum still detectable concentration N_i of absorbing molecule is determined by the absorption path length L , the absorption cross-section σ_{ik} , and the minimum detectable relative intensity change $\Delta I/I_0$ caused by absorption.

In order to reach a high detection sensitivity for absorbing molecules, i.e., reach a low minimum still detectable concentration, $L \cdot \sigma_{ik}$ should be large and the minimum detectable value of $\Delta I/I_0$ as small as possible.

- ① To get large σ_{ik} , if possible, choose the transition with large absorption cross section. For example, Na D_1 and D_2 transitions — choose D_2 as it has double σ_{ik} than D_1 line, (due to degeneracy factor).
- ② In many occasions, σ_{ik} is fixed (due to available laser source, atom/molecule conditions, etc), In order to have high sensitivity, a good approach is to increase the absorption path length. Here comes the multi-passes

design, i.e., let the laser light go back and forth between cavity mirrors many times to increase the absorption path length.

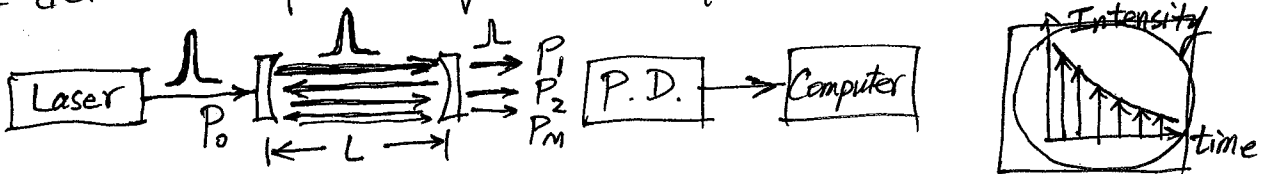


$$L_{\text{effective}} = 2nL \quad (10)$$

n times round-trip

Here, the shadow means the part of mirror with 100% reflectivity. Of course, this is an ideal situation — not really possible in reality, because $R < 100\%$ usually, e.g., 99.99%. There are always some losses in the mirrors.

§14.2. Cavity Ring down Spectroscopy is based on this multipass idea, but further developed to utilize the detection of decay time of transmitted light intensity.



Assume a short laser pulse with input power P_0 is sent through an optical resonator with two highly reflecting mirrors. The pulse will be reflected back and forth between the mirrors, while for each round-trip a small fraction will be transmitted through the end mirror and reach the detector. Assume mirror reflectivities $R_1 = R_2 = R$, mirror transmission $T = 1 - R - A \ll 1$, where A includes all losses of the cavity from absorption, scattering, and diffraction, except those losses introduced by the absorbing sample. Assume sample absorption coefficient is α .

The transmitted power of the first output pulse is

$$P_1 = P_0 \cdot T \cdot e^{-\alpha L} \cdot T = P_0 \cdot T^2 e^{-\alpha L} \quad (11)$$

The 2nd output pulse power is

$$\begin{aligned} P_2 &= P_0 \cdot T \cdot e^{-\alpha L} \cdot R \cdot e^{-\alpha L} \cdot R \cdot e^{-\alpha L} \cdot T \\ &= P_0 \cdot T^2 e^{-\alpha L} \cdot [R^2 e^{-2\alpha L}] \end{aligned} \quad (12)$$

i.e., for each round-trip, the pulse power decreases by an additional factor $(R^2 e^{-2\alpha L})$. Thus, after n round-trips, the power of transmitted pulse becomes

$$P_{n+1} = P_0 \cdot T^2 \cdot e^{-\alpha L} [R e^{-\alpha L}]^{2n} = P_1 [(1-T-A) e^{-\alpha L}]^{2n} \quad (13)$$

which can be written as

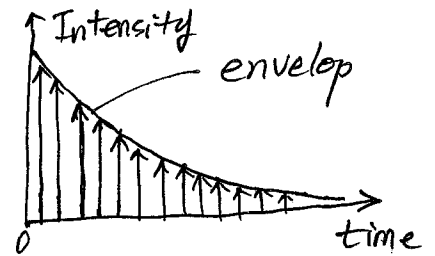
$$\begin{aligned} P_{n+1} &= P_1 \cdot e^{2n(\ln R - \alpha L)} = P_1 \cdot e^{2n[\ln(1-T-A) - \alpha L]} \\ &\approx P_1 e^{-2n[T+A+\alpha L]} \end{aligned} \quad (14)$$

The time delay between successive transmitted pulses equals the cavity round-trip time $T_R = 2L/c$ (here we regard medium refraction index as 1). The n th pulse is therefore detected at the time $t = 2nL/c$. From Eq. (14), we have

$$\therefore P(t = 2nL/c) = P_1 e^{-\frac{2nL/c}{\frac{L/c}{T+A+\alpha L}}} = P_1 e^{-t/\tau_1} \quad (15)$$

where $\tau_1 = \frac{L/c}{T+A+\alpha L} = \frac{L/c}{1-R+\alpha L}$ (16) is the decay time.

If the detector time constant is really small (ie, very fast detector), then we may see each individual pulses sequentially coming out the cavity. But usually the detector used in CRDS is slow detector (with long time constant). Thus, the detector averages over subsequent pulses and obtains the envelop of the decay pulses.



Without the absorbing sample, the decay time $\tau_2 = \frac{L/c}{T+A}$ (17)

∴ Decay time difference

$$\Delta\tau = \tau_2 - \tau_1 = \frac{L/c \cdot \alpha L}{(T+A)(T+A+\alpha L)} = \frac{\alpha \cdot L^2/c}{(T+A)(T+A+\alpha L)}$$

$$= \frac{\alpha \cdot L^2/c}{(1-R)(1-R+\alpha L)} \quad (18)$$

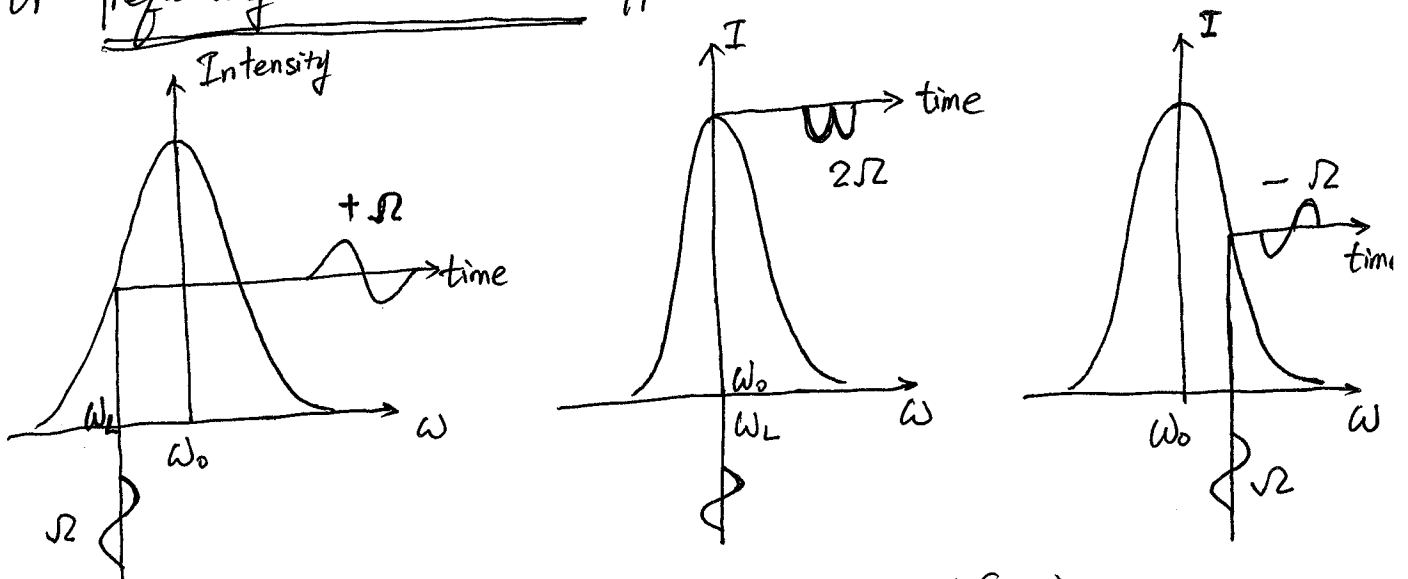
$$= \frac{\alpha \cdot L \cdot \tau_1}{1-R}$$

$$\Rightarrow \alpha = \frac{\Delta\tau}{\tau_1} \cdot \frac{1-R}{L} \quad (19)$$

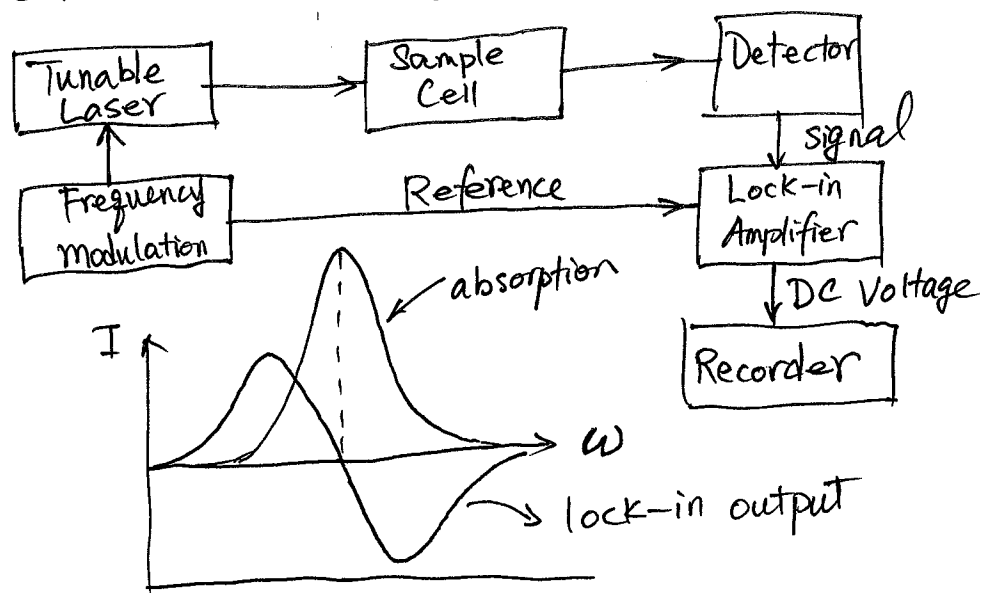
Thus, the absorption coefficient α can be determined from the decay time measurements. The minimum detectable absorption coefficient α is determined by the reflectivity R of the cavity mirrors and the accuracy of the decay time measurements.

③ $\Delta I/I_0$ is limited by noise level. If we can somehow reduce the noise in detection, $\Delta I/I_0$ can be measured to very small amount and dramatically improve detection sensitivity.

There are many ways to reduced noise and improve detection sensitivity. One of them is to change DC detection to AC detection, using wavelength-modulation or frequency-modulation approach.

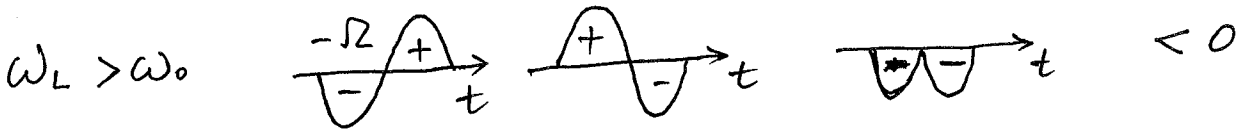
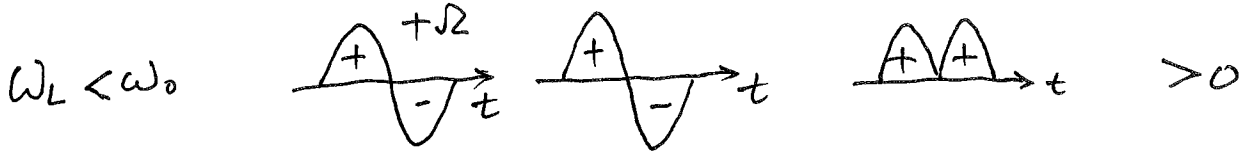
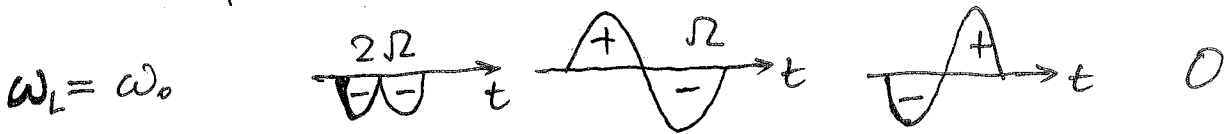


In phase-sensitive detection (lock-in amplifier)

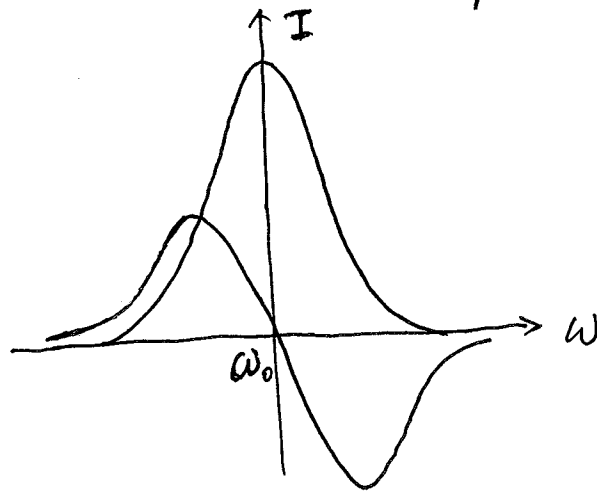


At lock-in amplifier

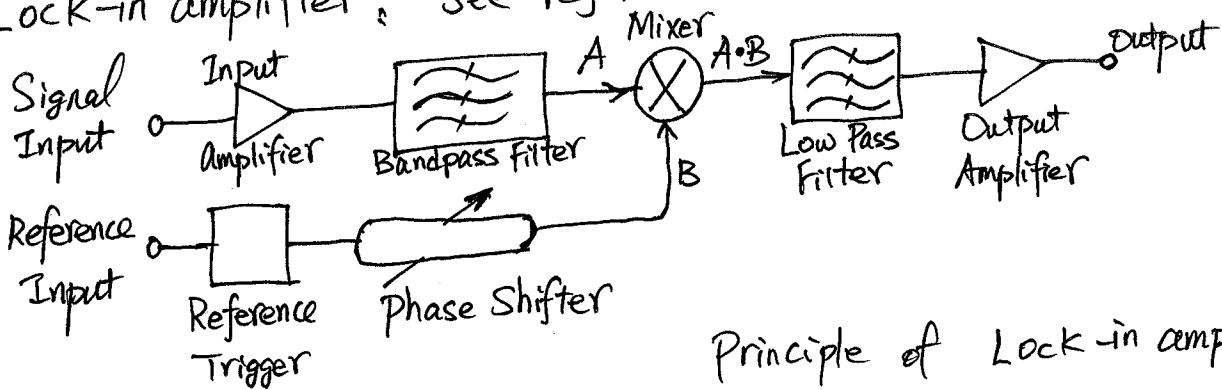
Input: signal \times reference = output \Rightarrow average



\therefore For an absorption line, the lock-in amplifier output is a derivative to the absorption line.

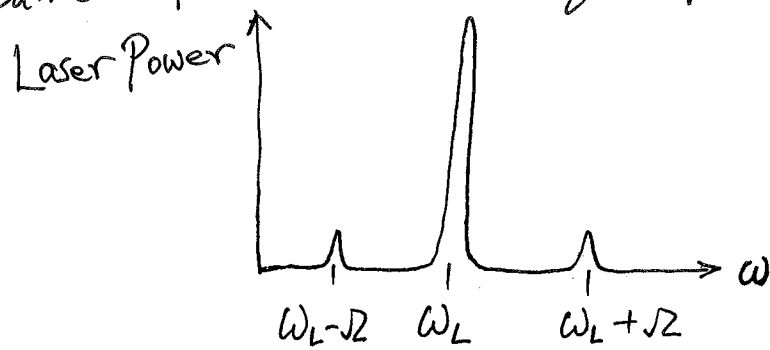


Lock-in amplifier, see references sent earlier through email.



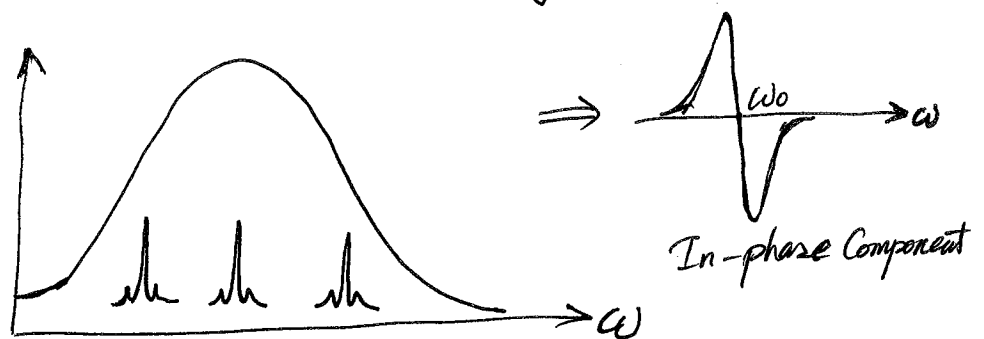
Principle of Lock-in amplifier.

Above is from the time domain to look at the signals. In frequency domain, the modulation causes the sidebands of the laser frequency:



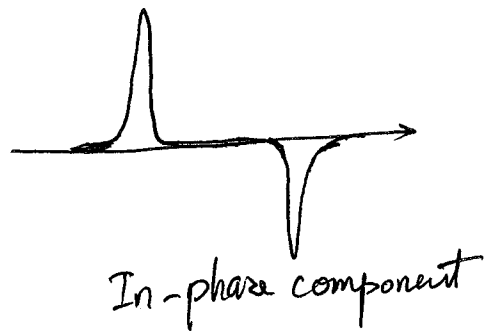
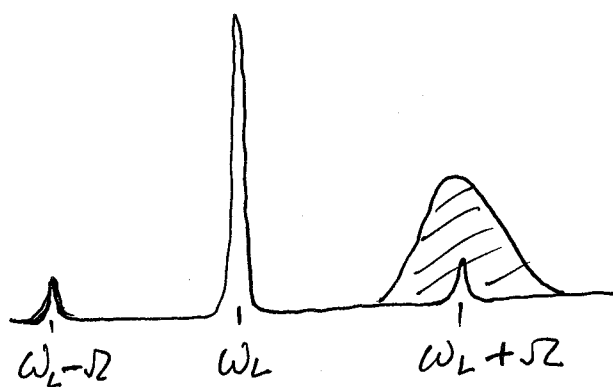
Three frequencies $\omega_L \pm \Delta$, ω_L interact with the sample and we detect the overall effect.

* If $\Delta \ll \Delta\omega_{\text{abs}}$, i.e., frequency modulation is much smaller than the absorption linewidth, then all ~~three~~ frequencies will interact with the absorbing sample simultaneously. — This is wavelength modulation.



By adjusting the phase between the reference and signal, the lock-in output is the first derivative of the absorption line (in-phase component, $\cos \Delta t$) or to the 2nd derivative of the dispersion ($\sin \Delta t$).

* If $\Omega \gg \Delta\omega_{\text{abs}}$, i.e., frequency modulation is much larger than the absorption linewidth, then we can make only one side band (e.g., $\omega_L + \Omega$) interact with the absorbing sample. — This is frequency modulation.



Through detailed mathematic derivation, we can show that there are in-phase component and quadratic component. Now the in-phase component can actually show the absorption line shape.

④ In case of very small values of αL , the detection of the attenuation of transmitted light intensity cannot be very accurate, since it must determine a small difference $I_0 - I_T$ of two large quantities I_0 and I_T . Small fluctuation of I_0 or of the splitting ratio of the beam splitter can severely influence the measurement.

To avoid this kind of problem, instead of measuring the attenuation, we can measure the increase of fluorescence the photoacoustic, optothermal, ionization, and optogalvanic effects. Among them, fluorescence excitation spectroscopy, especially Laser Induced Fluorescence (LIF), is the major approach in modern spectroscopy, especially in lidar/optical remote sensing. See textbook for details.

⑤ Intracavity or external resonator is another way to improve absorption length or fluorescence intensity, thus, resulting in high detection sensitivity.
(See textbook for details)