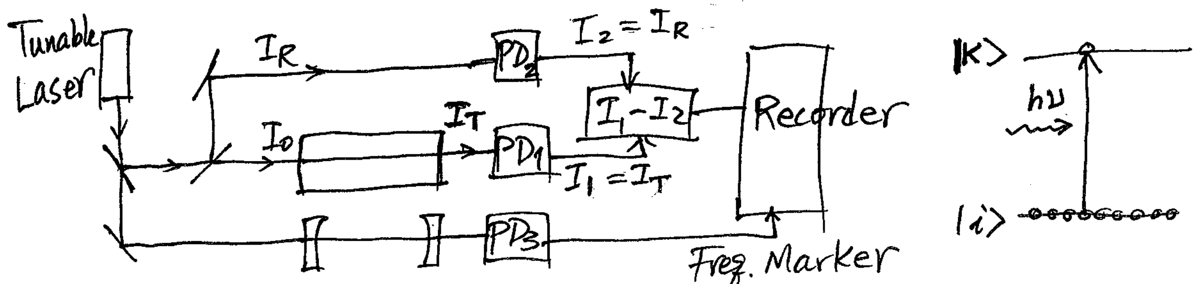
Chapter 14. Doppler-Limited Absorption and Fluorescence Spectroscopy

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: $I_T(\omega) = I_0 e^{-\alpha(\omega) L}$ (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.,

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

Taking the difference between the two channels, we have

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

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

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

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

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

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

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).

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

$N_K \to 0$ when $E_K \gg E_i$

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

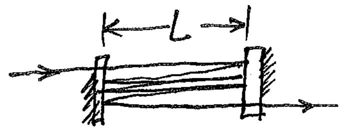
where $\Delta I = I_0 - I_T$, L is the absorption length.

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 occassions, 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.

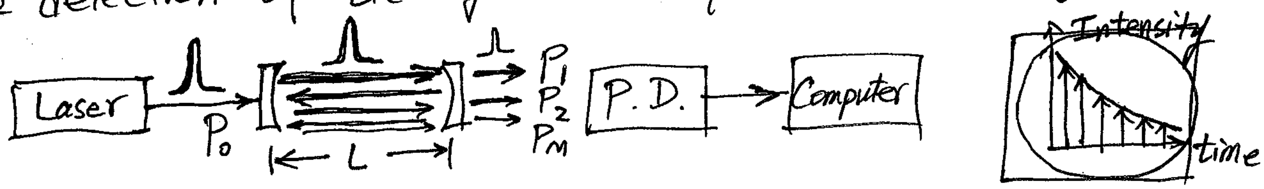


$$L_{effective} = 2nL \quad (10)$$

n times round-trip

Here, the shawdow 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. <u>Cavity Ring down Spectroscopy</u> 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

$$P_2 = P_0 \cdot T \cdot e^{-\alpha L} \cdot R \cdot e^{-\alpha L} \cdot R \cdot e^{-\alpha L} \cdot T$$
$$= P_0 \cdot T^2 e^{-\alpha L} \cdot \left[R^2 e^{-2\alpha L}\right] \quad (12)$$

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

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

which can be written as

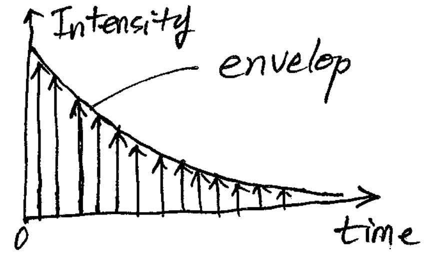
$$P_{n+1} = P_1 \cdot e^{2n(\ln R - \alpha L)} = P_1 \cdot e^{2n[\ln(1-T-A) - \alpha L]}$$
$$\approx P_1 e^{-2n[T+A+\alpha L]} \quad (14)$$

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 nth pulse is therefore detected at the time $t = 2nL/c$. From Eq (14), we have

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

where $\tau_1 = \dfrac{L/c}{T+A+\alpha \cdot L} = \dfrac{L/c}{1-R+\alpha L}$ (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)

$\therefore$ Decay time difference

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

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

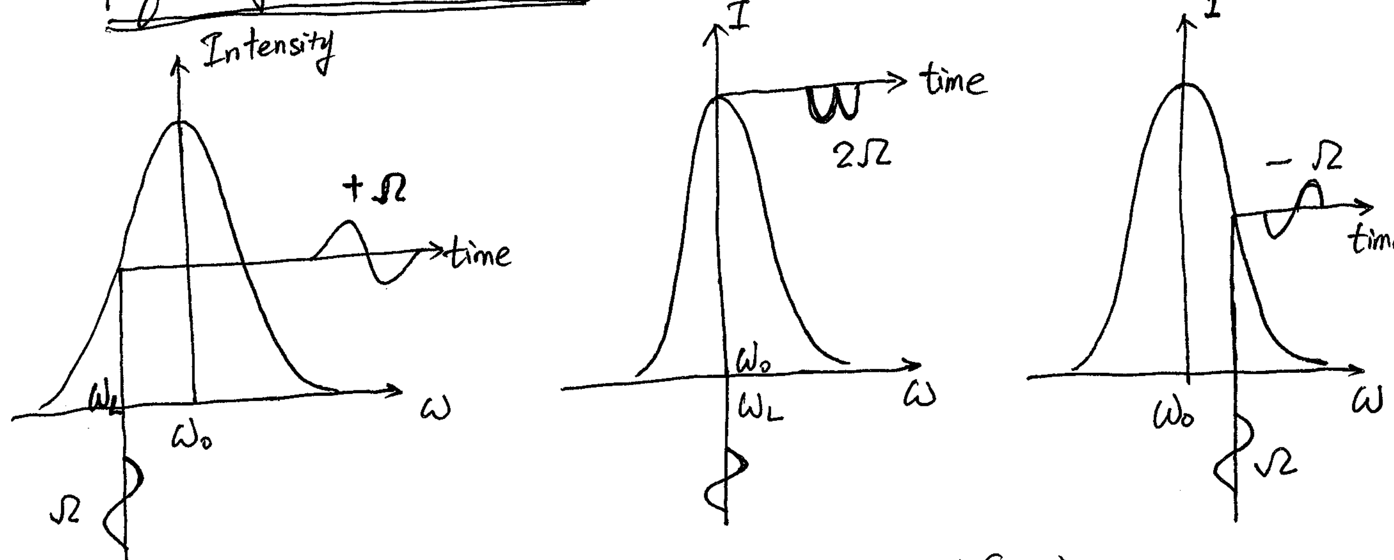
$$= \frac{\alpha \cdot L \cdot \tau_1}{1-R}$$

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

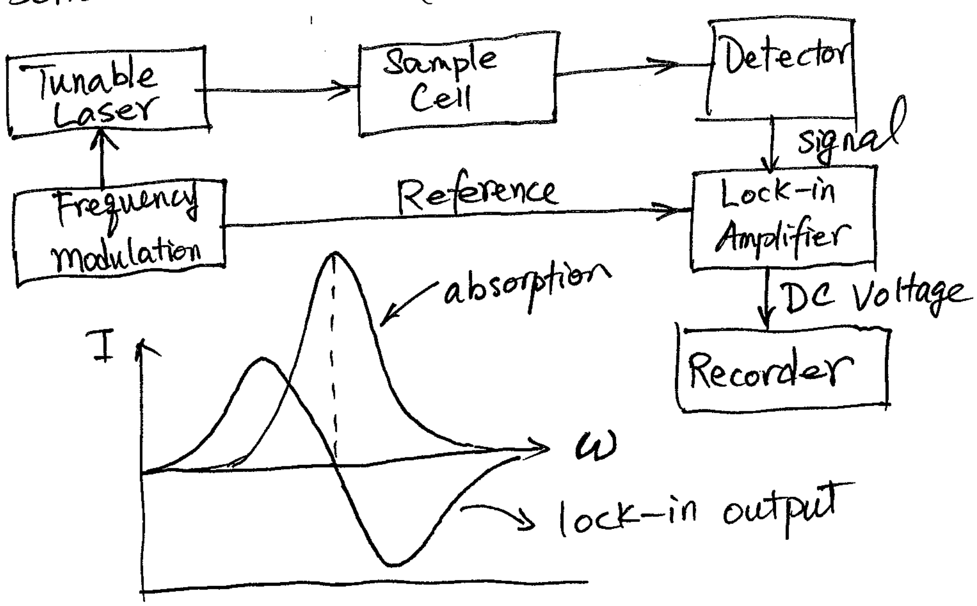
Thus, the absorption coefficient α can be determined from the decay time measurements. The minimum detectable absorption coefficient α is determined by the reflectivity R of the cavity mirrors and the accuracy of the decay time measurements.

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.

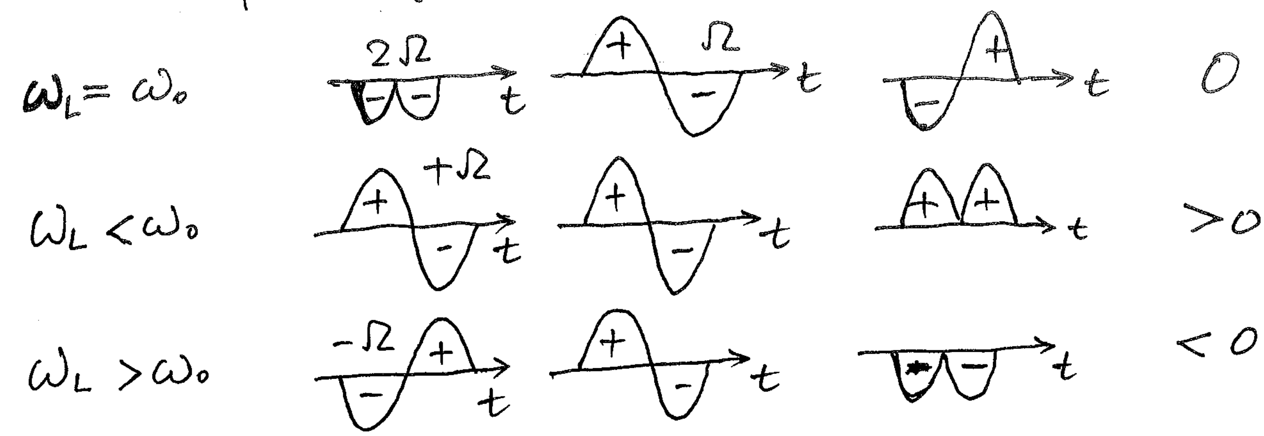


In phase-sensitive detection (lock-in amplifier)

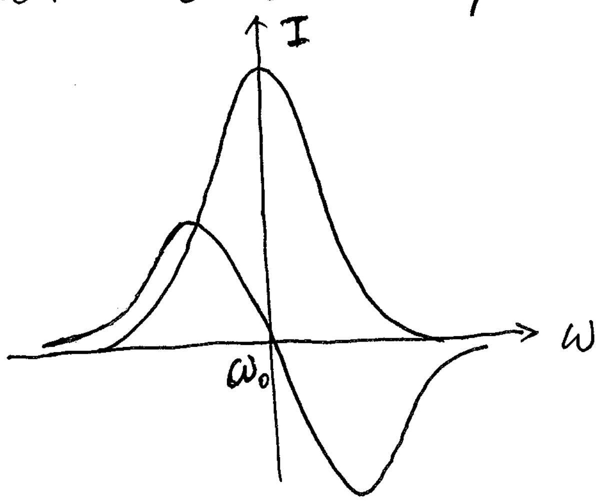


At lock-in amplifier

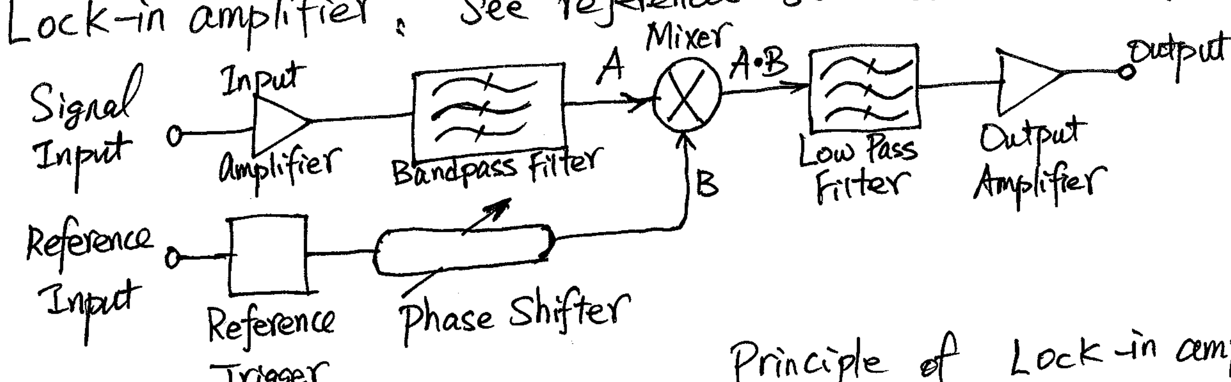
Input : signal × reference = output ⇒ average



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

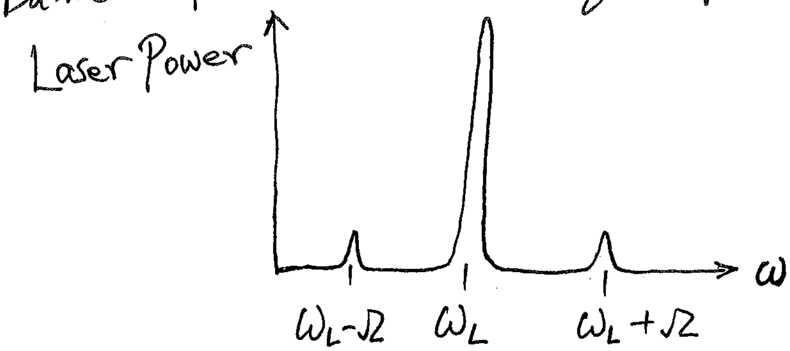


Lock-in amplifier. See references sent earlier through email.



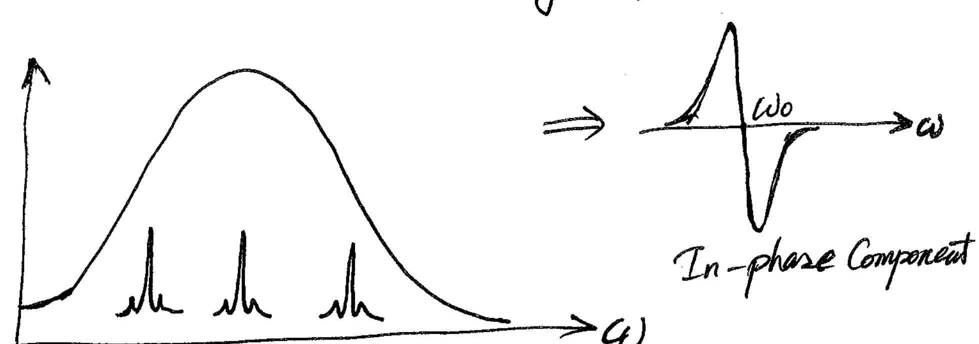
Principle of Lock-in amplifier.

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



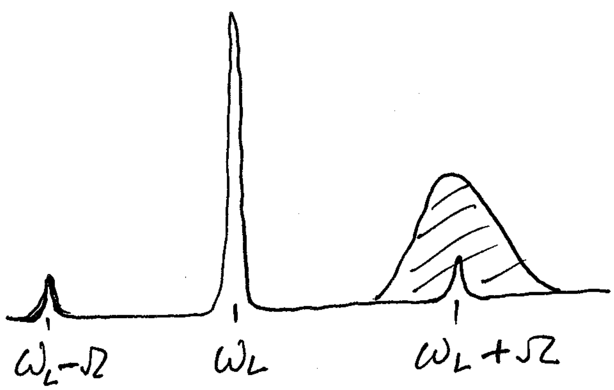
Three frequencies $\omega_L \pm \Omega$, ω_L interact with the sample and we detect the overall effect.

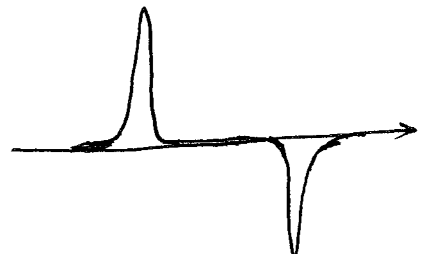
* If $\Omega \ll \Delta\omega_{abs}$, i.e., frequency modulation is much smaller than the absorption linewidth, then all ~~three~~ frequencies will interact with the absorbing sample simultaneously. —— This is wavelength modulation.



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

* If $\Omega \gg \Delta\omega_{abs}$, 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.





In-phase component

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.

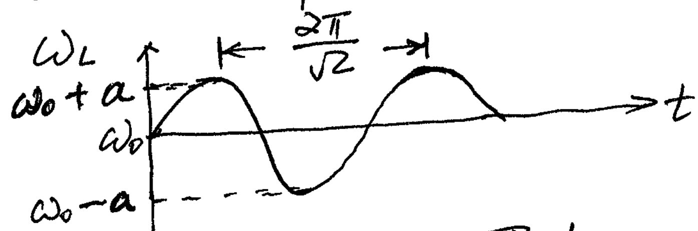
⑤ Intracavity or external resonator is another way to improve absorption length or fluorescence intensity, thus, resulting in high detection sensitivity.
(See textbook for details)

Frequency Modulation Spectroscopy

The laser frequency ω_L is modulated at the modulation frequency Ω according to the following relationship: (e.g., changing laser cavity length periodically)

$$\omega_L(t) = \omega_0 + a \sin \Omega t \quad (20)$$

where a is the amplitude that the laser frequency is modulated.



If a is sufficiently small, Taylor expansion $\boxed{\text{let } a = \Delta\omega_L}$

$$I_T(\omega_L + \Delta\omega_L) - I_T(\omega_L) = \frac{dI_T}{d\omega}\Delta\omega_L + \frac{1}{2!}\frac{d^2 I_T}{d\omega^2}\Delta\omega_L^2 + \cdots \quad (21)$$

From Eq. (5) $\alpha(\omega) = \dfrac{I_0 - I_T}{I_0 L}$, we have ($I_0$ is constant)

$$\frac{d\alpha(\omega)}{d\omega} = -\frac{1}{I_0 L}\frac{dI_T}{d\omega} \quad (22)$$

$\therefore$ $dI_T/d\omega$ is proportional to the 1st derivative of the absorption $\alpha(\omega)$.

With ω_L modulation, Taylor expansion gives

$$I_T(\omega_L) = I_T(\omega_0) + \sum_n \frac{a^n}{n!} \sin^n \Omega t \left(\frac{d^n I_T}{d\omega^n}\right)_{\omega_0} \quad (23)$$

For $\alpha L \ll 1$, from Eq. (2), $I_T = I_0 e^{-\alpha L} \approx I_0[1 - \alpha L]$

$$\therefore \left(\frac{d^n I_T}{d\omega^n}\right)_{\omega_0} = -I_0 L\left(\frac{d^n \alpha(\omega)}{d\omega^n}\right)_{\omega_0} \quad (24)$$

Convert $\sin^n \Omega t$ into linear function of $\sin(n\Omega t)$ and $\cos(n\Omega t)$.

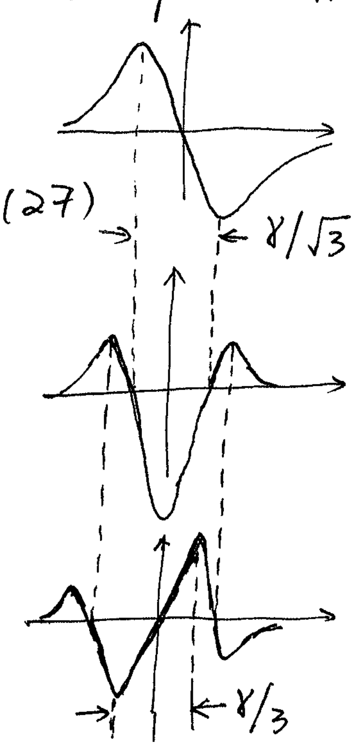
$$\frac{I_T(\omega_L)-I_T(\omega_0)}{I_0} = -aL\Big\{\Big[\frac{a}{4}\Big(\frac{d^2\alpha}{d\omega^2}\Big)_{\omega_0} + \frac{a^3}{64}\Big(\frac{d^4\alpha}{d\omega^4}\Big)_{\omega_0} + \cdots\Big]$$
$$+\Big[\Big(\frac{d\alpha}{d\omega}\Big)_{\omega_0} + \frac{a^2}{8}\Big(\frac{d^3\alpha}{d\omega^3}\Big) + \cdots\Big]\sin(\Omega t)$$
$$+\Big[-\frac{a}{4}\Big(\frac{d^2\alpha}{d\omega^2}\Big)_{\omega_0} + \frac{a^3}{48}\Big(\frac{d^4\alpha}{d\omega^4}\Big)_{\omega_0} + \cdots\Big]\cos(2\Omega t)$$
$$+\Big[-\frac{a^2}{24}\Big(\frac{d^3\alpha}{d\omega^3}\Big)_{\omega_0} + \frac{a^4}{384}\Big(\frac{d^5\alpha}{d\omega^5}\Big)_{\omega_0} + \cdots\Big]\sin(3\Omega t)$$
$$+\cdots\Big\}. \qquad (25)$$

For a sufficiently small frequency-modulation amplitude ($a/\omega_0 \ll 1$), the 1st term in each bracket are dominant. Therefore, behind a lock-in amplifier tuned to the frequency $n\Omega$, we obtain the signal $S(n\Omega)$ for freq. $n\Omega$:

$$S(n\Omega) = \left(\frac{I_T(\omega_L)-I_T(\omega_0)}{I_0}\right)_{n\Omega} = aL\begin{cases} b_n \sin(n\Omega t), & \text{for } n=2m+1 \text{ (odd order)} \\ C_n \cos(n\Omega t), & \text{for } n=2m \text{ (even order)} \end{cases} \qquad (26)$$

The signal for the first three derivatives of the absorption coefficient $\alpha(\omega)$ are

$$\left.\begin{aligned} S(\Omega) &= -aL\frac{d\alpha}{d\omega}\sin(\Omega t) \\ S(2\Omega) &= +\frac{a^2L}{4}\frac{d^2\alpha}{d\omega^2}\cos(2\Omega t) \\ S(3\Omega) &= +\frac{a^3L}{24}\frac{d^3\alpha}{d\omega^3}\sin(3\Omega t) \end{aligned}\right\} (27)$$



$$\alpha(\omega) = A\frac{\gamma}{(\omega-\omega_0)^2+(\gamma/2)^2} \qquad (28)$$

The advantage of this "derivative spectroscopy" with frequency-modulated laser is the possibility for phase-sensitive detection, which restricts the frequency response of the detection system to a narrow frequency interval centered at the modulation frequency Ω.

— Frequency-independent background absorption from cell windows and background noise from fluctuations of the laser intensity or of the density of absorbing molecules are essentially reduced.

— Laser frequency can be modulated by applying an AC voltage or ramp voltage to the piezo onto which a resonator mirror is mounted, i.e., by modulating the laser cavity length.

— The technical noise, which represents the major limitation, decreases with increasing frequency. It is advantageous to choose the modulation frequency as high as possible.

* For this kind of frequency modulation by modulating laser cavity length, the modulation frequency cannot be high, because piezo cannot response to high frequency modulation. Thus, this is low frequency (Ω) modulation, and at each moment, the laser output frequency is regarded as a single frequency without sidebands. In this case, the modulation amplitude $a (= \Delta\omega_L)$ matters, while the modulation frequency Ω is just how fast you modulate ω_L.

(how much you can deviate from ω_L frequency)

The laser frequency does shift between ω_0 and $\omega_0 \pm a$.
When $\omega_L = \omega_0 + a \sin\Omega t$, there is no component staying at ω_0.

To achieve better performance, i.e., high frequency modulation, phase-modulated spectroscopy can be used. For normal lasers, an electro-optical modulators outside the laser resonator are used as phase modulators, resulting in a frequency modulation of the transmitted laser beam. For diode lasers, high frequency modulation can be achieved by modulating the diode current. When the modulation frequency is relatively low, this can be regarded as direct frequency modulation. When the modulation frequency is high ($\geqslant 5$ MHz), the diode itself functions as an EO crystal, thus, it should be regarded as phase modulation, resulting in the frequency modulation of the diode laser beam. (Diode laser is a special case!)

Phase modulation cannot be separated from frequency modulation. The instantaneous frequency of a periodic signal is defined as the time derivative of the overall phase of the signal, i.e.,

$$2\pi f(t) \equiv \frac{d\Phi(t)}{dt} = \omega + \frac{d\phi(t)}{dt} \qquad (29)$$

Where $f(t)$ is the instantaneous frequency, $\phi(t)$ is the signal's global phase, and ω is the optical angular frequency.

Given a phase modulation $\phi(t) = m \sin \Omega(t)$ (30)

Where m is the phase-modulation index, sinusoidal phase modulation result in sinusoidal frequency modulation at a fixed frequency Ω, but with a $90°$ phase lag and a peak-to peak excursion of $2m\Omega$.

The phase-modulated field amplitude can be represented as a set of Fourier components in which power exists only at the discrete optical angular frequencies $\omega \pm k\Omega$:

$$E_{pm} \equiv E_0 e^{i[\omega t + m \sin \Omega t]}$$

$$\equiv E_0 \left\{ \sum_{k=0}^{\infty} J_k(m) e^{ik\Omega t} + \sum_{k=0}^{\infty} (-1)^k J_k(m) e^{-ik\Omega t} \right\} e^{i\omega t} \qquad (31)$$

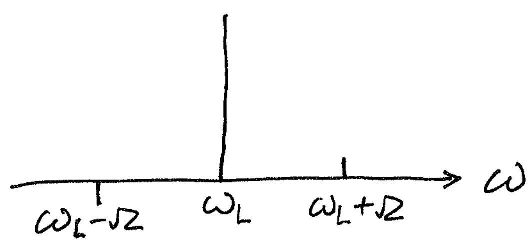
where k is an integer, m is the phase-modulation index, i.e., the modulation depth, and $J_k(m)$ is the ordinary Bessel function of order k.

In the case of small modulation index, $m \ll 1$, then only the $k=0$ and $k=1$ terms are significant. So the expansion (31) reduces to:

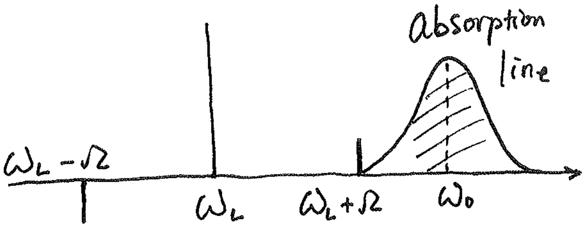
$$E_{pm} \approx E_0 [1 + im \sin \Omega t] e^{i\omega t} \qquad (32)$$

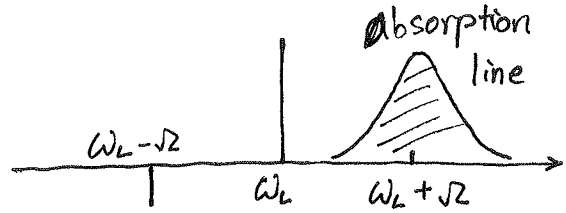
Here, most of the optical power resides in the Fourier component called the "carrier", at frequency ω, with a small amount of optical power in the two first-order side bands at frequencies $\omega \pm \Omega$.

[Reference: New Focus Application Note 2]

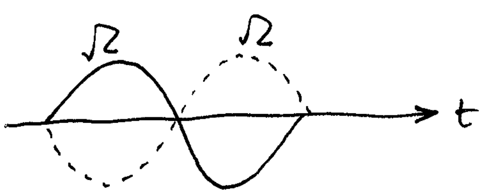


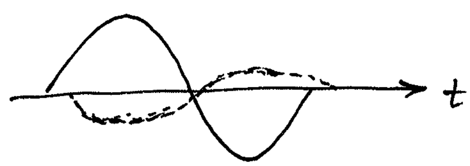
The phase modulation has an additional advantage: the first two sidebands at frequencies $\omega + \Omega$ and $\omega - \Omega$ have equal amplitudes but opposite phases (above figure). A lock-in detector tuned to the modulation frequency Ω receives the superposition of two beat signals between the carrier and the two sidebands, which cancel to zero if no absorption is present. Any fluctuation of the laser intensity appears equally on both signals and is therefore also cancelled.





If $\Omega > \Delta\omega_{abs}$ (where $\Delta\omega_{abs}$ is the width of the absorption line) and the laser wavelength is tuned over an absorption line, we can make only one side band (e.g., $\omega_L + \Omega$) interact with the absorbing sample. Thus, one sideband is absorbed. This perturbs the balance and gives rise to a signal with a profile that is similar to the profile of the second derivative.





See paper by G.C. Bjorklund
"Frequency Modulation (FM) Spectroscopy – Theory of Lineshapes and Signal-to-Noise Analysis", Applied Phys. B 32, 145-152, 1983.

{ Direct Frequency Modulation
Phase-Modulated Frequency Modulation

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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)

$$\Delta P(\omega) = \alpha(\omega) L P_{int} = g\,\alpha(\omega) L P_{out}$$

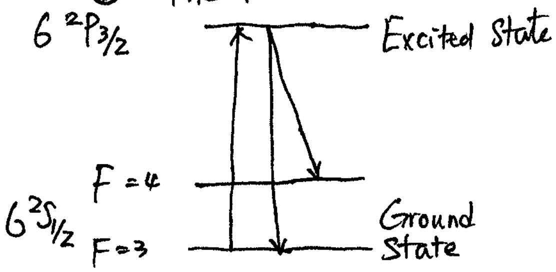
monitoring pressure increase in the cell or laser-induced fluorescence

§14.3. Optical Pumping and Double-Resonance (Textbook Chapter 10)

Optical pumping method was invented by Alfred Kastler in 1950s. Alfred Kastler was a French physicist. He won Nobel Prize in 1966.

Optical pumping has several different aspects:

① The increase or decrease of the population in selected levels (Ground states), using selective excitation.



If the incident light only excites population on $F=3$, but the excited atoms can go to $F=3$ and $F=4$ levels. Then after a while, nearly all populations will be at $F=4$, while $F=3$ is nearly depleted. This results in huge population difference between $F=3$ and $F=4$, enabling magnetic resonance transitions.

② Increase population in selected excited states by intense laser pumping → laser induced fluorescence as a better light source

→ allowing study of transitions from this excited state to higher-lying levels.

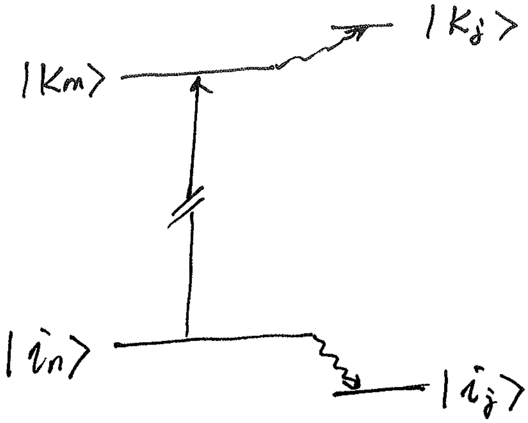
→ If laser is narrow enough, selected velocity group of atoms are excited → yielding Doppler-free double-resonance signal.

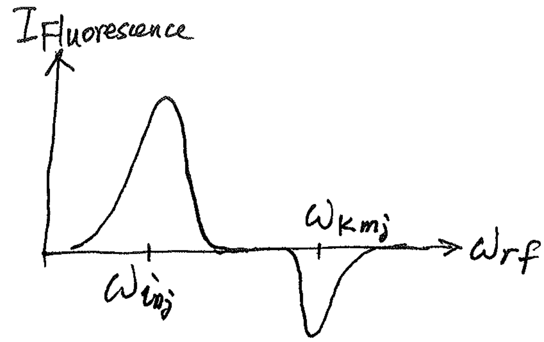
③ Selective population or depletion of degenerated M sublevels

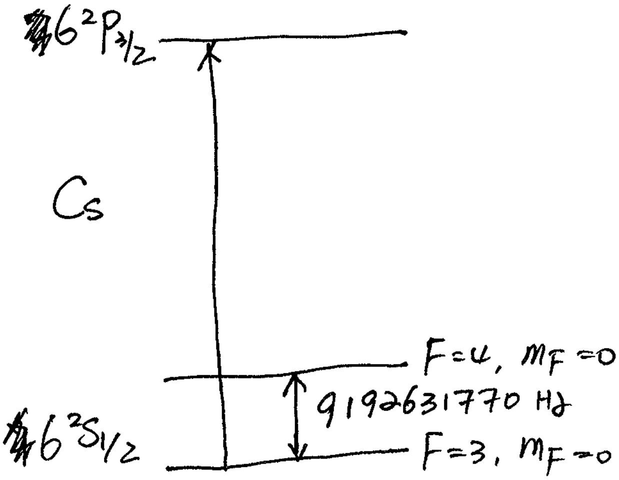
→ alignment.

④ Coherent excitation of two or more molecular levels → producing definite phase relations between the wave functions of these levels.

Double - Resonance Technique







Cs clock using laser pumping and probing.