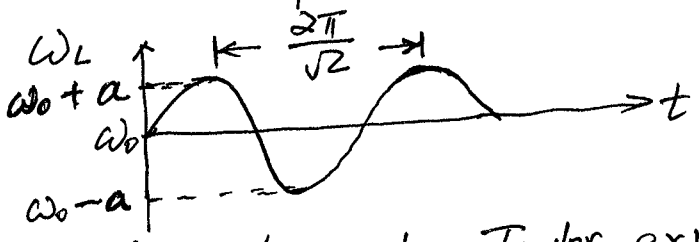
Frequency Modulation Spectroscopy

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

$$\omega_L(t) = \omega_0 + a\sin\Omega t \tag{20}$$

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



If a is sufficiently small, Taylor expansion (let $a = \Delta\omega_L$)

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

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

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

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

With ω_L modulation, Taylor expansion gives

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

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

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

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

$$\frac{I_T(\omega_L)-I_T(\omega_0)}{I_0} = -aL\left\{\left[\frac{a}{4}\left(\frac{d^2\alpha}{d\omega^2}\right)_{\omega_0} + \frac{a^3}{64}\left(\frac{d^4\alpha}{d\omega^4}\right)_{\omega_0} + \cdots\right]\right.$$

$$+\left[\left(\frac{d\alpha}{d\omega}\right)_{\omega_0} + \frac{a^2}{8}\left(\frac{d^3\alpha}{d\omega^3}\right) + \cdots\right]\sin(\Omega t)$$

$$+\left[-\frac{a}{4}\left(\frac{d^2\alpha}{d\omega^2}\right)_{\omega_0} + \frac{a^3}{48}\left(\frac{d^4\alpha}{d\omega^4}\right)_{\omega_0} + \cdots\right]\cos(2\Omega t)$$

$$+\left[-\frac{a^2}{24}\left(\frac{d^3\alpha}{d\omega^3}\right)_{\omega_0} + \frac{a^4}{384}\left(\frac{d^5\alpha}{d\omega^5}\right)_{\omega_0} + \cdots\right]\sin(3\Omega t)$$

$$\left. + \cdots \right\}. \qquad (25)$$

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. $n\Omega$:

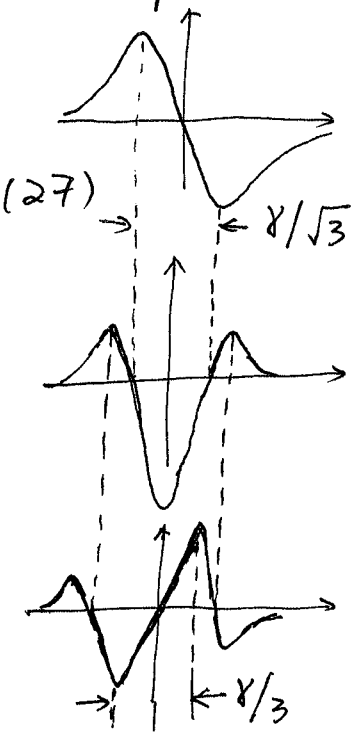
$$S(n\Omega) = \left(\frac{I_T(\omega_L)-I_T(\omega_0)}{I_0}\right)_{n\Omega} = aL\begin{cases} b_n \sin(n\Omega t), & \text{for } n=2m+1 \text{ (odd order)} \\ C_n \cos(n\Omega t), & \text{for } n=2m \text{ (even order)} \end{cases} \qquad (26)$$

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

$$S(\Omega) = -aL\frac{d\alpha}{d\omega}\sin(\Omega t)$$

$$S(2\Omega) = +\frac{a^2L}{4}\frac{d^2\alpha}{d\omega^2}\cos(2\Omega t) \qquad (27)$$

$$S(3\Omega) = +\frac{a^3L}{24}\frac{d^3\alpha}{d\omega^3}\sin(3\Omega t)$$



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

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. (a: 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 (≥ 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 $\omega \pm k\Omega$:

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

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

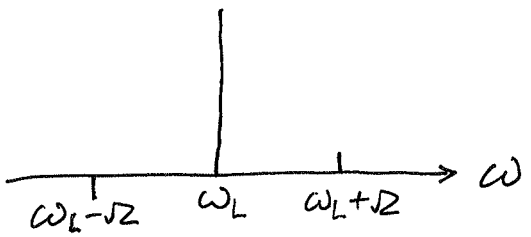
where k is an integer, m is the phase-modulation index, i.e., the modulation depth, and $J_k(m)$ is the ordinary Bessel function of order k.

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:

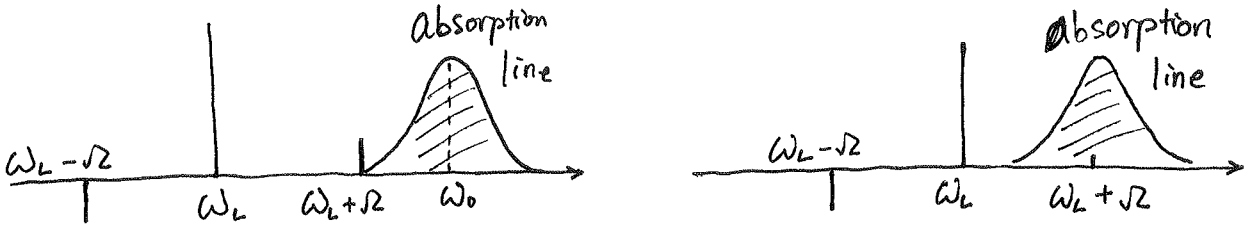
$$E_{pm} \approx E_0 [1 + im\sin\Omega t] e^{i\omega t} \qquad (32)$$

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 sidebands 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 sideband (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

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)

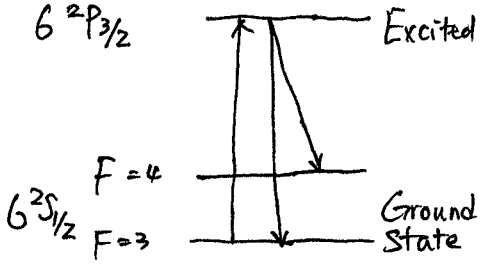
$$\Delta P(\omega) = \alpha(\omega) L P_{int} = \mathcal{F} \alpha(\omega) L P_{out}$$

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, using selective excitation.



Ground states

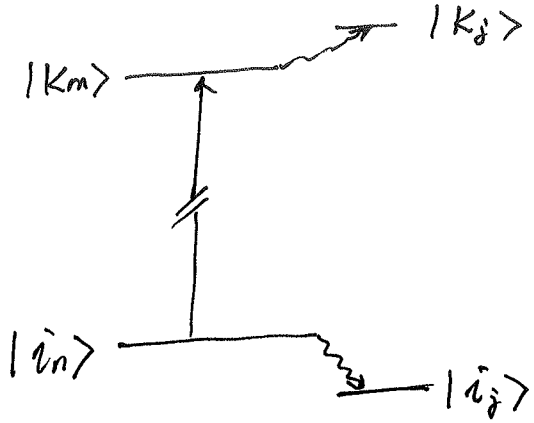
If the incident light only excites population on F=3, but the excited atoms can go to F=3 and F=4 levels. Then after a while, nearly all populations will be at F=4, while F=3 is nearly depleted. This results in huge population difference between F=3 and F=4, enabling magnetic resonance transitions.

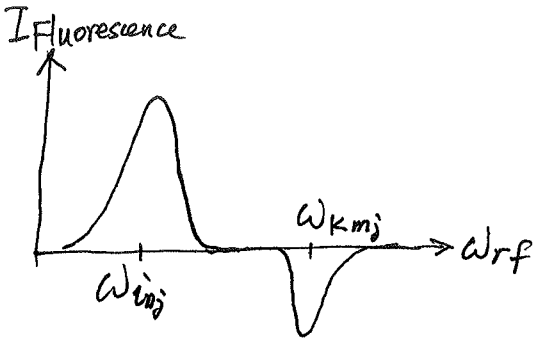
② Increase population in selected excited states by intense laser pumping → laser induced fluorescence as a better light source
→ allowing study of transitions from this excited state to higher-lying levels.
→ If laser is narrow enough, selected velocity group of atoms are excited → yielding Doppler-free double-resonance signal.

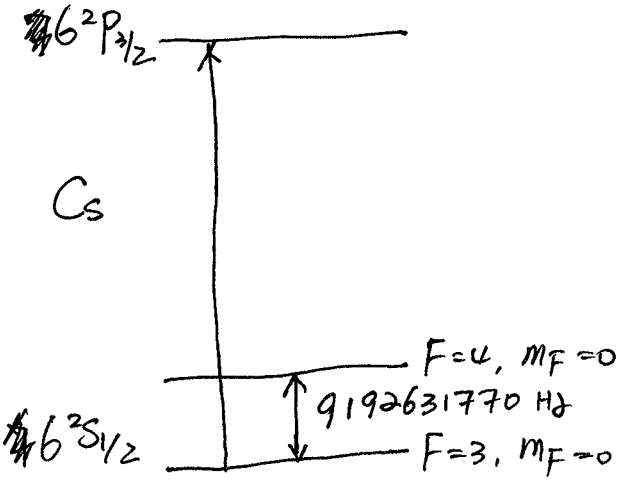
③ Selective population or depletion of degenerated M sublevels → alignment.

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.