Chapter 15. Doppler-Free Laser Spectroscopy

Reference: Textbook "Laser Spectroscopy" Chapters 7, 9, and 14.

In this section, we deal with various approaches on how to improve spectral resolution. The goal is to obtain high spectral resolution in order to distinguish more spectral lines that may be otherwise undistinguishible under Doppler limit. It is also used to obtain narrow spectral line profiles that have wide applications in spectroscopy and laser freq. control and locking. Since the major broadening mechanism in most cases is the Doppler broadening, which is an inhomogeneous broadening as we discussed in atomic spectroscopy, the major approaches discussed in this section is how to "defeat" Doppler effect to obtain natural-linewidth-limited spectroscopy.

Recall that Doppler broadening is originated from Doppler effect, i.e., the Doppler shift caused by the velocity of atoms or molecules along the line of sight of the light beam. Under thermal equilibrium, atoms have Maxiwellian velocity distribution, so different velocity groups have different amounts of Doppler shift in frequency, resulting in the broadening of spectral line as what we measure are the statistical contribution of the atom ensemble.

Keep above message in mind, we can "defeat" Doppler-effect from several different aspects as summarized below.

A brief Summary for Doppler-free Spectroscopy.

(1) Velocity Selection Methods: only one velocity subgroup of atoms is selected to contribute to the signal. (Chapter 7)

① Saturation absorption Spectroscopy
② Intermodulation fluorescence Spectroscopy
} absorption coefficient change

③ Polarization spectroscopy → refraction index change

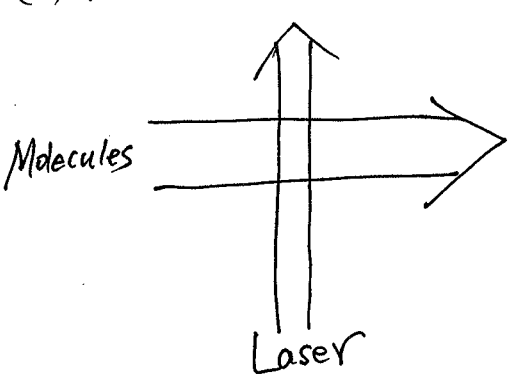
④ Velocity-selective optical pumping spectroscopy
↳ could use much lower laser power

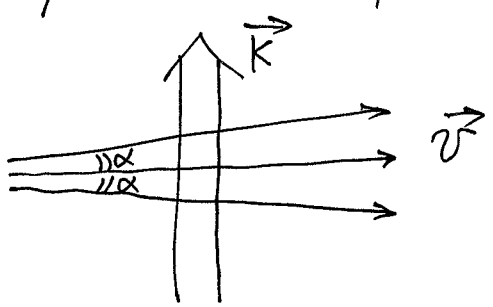
(2) Doppler-Effect Cancellation Methods: (Section 7.5)

Multiphoton Spectroscopy: two laser beams propagate oppositely, cancelling Doppler effect if absorbed by a molecule regardless its velocity ⇒ only when laser freq $\omega_L = \omega_0$, absorption occurs and for all molecules. Though 2-photon transition probability is low, all molecules contribute to the signal. Thus,

Signal $\propto P_{transition} \times N_{population} \approx$ Saturation spectr.

(3) Molecular Beam: prepare sample in a uniform velocity





(Chapter 9)

Residual Doppler shift:

$$2\vec{k}\cdot\vec{v} = 2kv\sin\alpha \approx 2kv\alpha$$

Since α is small, the residual Doppler broadening is much smaller than normal thermal Doppler broadening. It can be even smaller than transit-time broadening that is the major broadening mechanism in molecular beam spectroscopy.

(4) Velocity Reduction Methods: Cooling and Trapping. Significantly decrease molecule velocity to nearly zero, thus, dramatically reduce Doppler shift and Doppler broadening. (Chapter 14)

for both 1st and 2nd orders of Doppler shift.

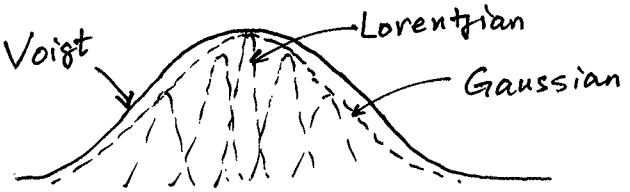
① Ion trap

② Laser cooling and trapping

One note: At each single laser frequency excitation, the resulted fluorescence usually has spectral distribution that is different than the laser spectrum or the molecular resonance frequency. However, we only detect the intensity / power / photon counts of the fluorescence, but not to distinguish the fluorescence spectrum. Thus, we record the overall fluorescence intensity versus the laser frequency, which can show sub-Doppler features owing to the Doppler-free feature of absorption.

§15.1. Saturation Spectroscopy and Polarization Spectroscopy

Doppler broadening is due to the contributions from different groups of atoms with different velocities. Each group of atoms has a Lorentzian lineshape determined by natural linewidth and collison broadening, whose center frequency has a shift relative to the resonance frequency of atoms at rest, depends on the velocity of this group of atoms (Doppler shift). For different groups of atoms, the central frequency shift is different, so these Lorentzian line-profiles spread out according to velocity, forming a near Gaussian profile (actually, a convolution of Lorentzian with Gaussian → Voigt profile).

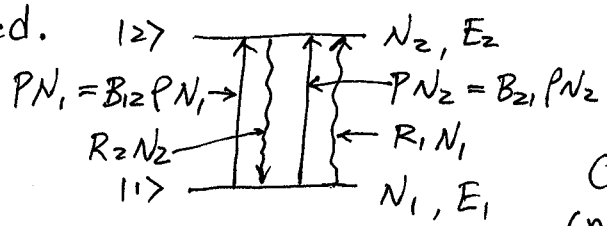


To improve spectral resolution, one idea is to select only one velocity group of atoms to form spectrum, thus, sub-Doppler line profile.

Saturation-Absorption Spectroscopy, Saturation-fluorescence spectroscopy, intermodulation fluorescence spectroscopy, and polarization spectroscopy are all based on the absorption of radiation field (photons) by atoms or molecules. Thus, we need to understand better of linear and nonlinear absorption.

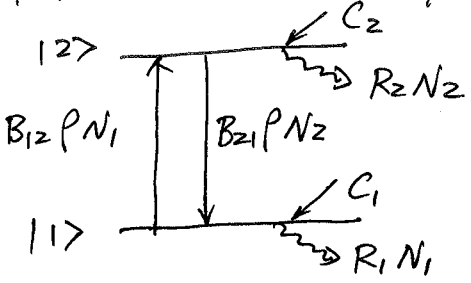
1. Linear and nonlinear absorption

In the Atomic Spectroscopy, we considered the linear and nonlinear absorption for a closed two-level system, i.e., the system only has two levels that are involved with the incident radiation, and all relaxations are still within these two levels, — no decay into other levels are allowed.

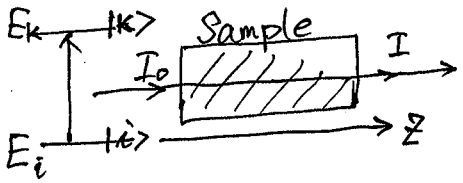


Closed 2-level system
(no decay into other levels)

Here we further consider an open two-level system, ie., channels are open for transitions out of the system and for the population of the system from outside.



Open 2-level system



From what we have learned in the atomic spectroscopy, the absorption effect can be expressed as:

$$dI = -I\alpha\, dz = -I\sigma_{ik}\left[N_i - \frac{g_i}{g_k}N_k\right]dz$$

$$= -I\sigma_{ik}\Delta N\, dz, \qquad (20)$$

where $\Delta N = \left[N_i - \frac{g_i}{g_k}N_k\right]$ is the difference of the population densities, α is the absorption coefficient (cm^{-1})

σ_{ik} is the absorption cross-section (cm^2)

N_i and N_k are the population densities on E_i and E_k,

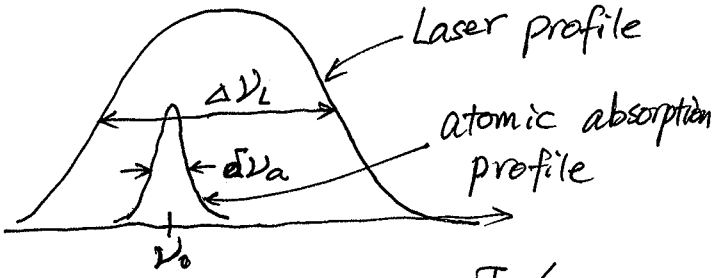
g_i and g_k are the degeneracy factors of E_i and E_k.

Eq.(20) is usually used for monochromatic radiation. Now if the incident laser has spectral energy density $\rho_\nu(\nu) = I_\nu(\nu)/c$ with the spectral width $\Delta\nu_L$, and the absorption line has the Full-width-at-half-maximum (FWHM) $\delta\nu_a$, then the intensity

change caused by the absorption is expressed as

$$dI = -dz \cdot \int I_\nu(\nu) \cdot \sigma_{ik}(\nu) \cdot \Delta N(\nu)\, d\nu. \qquad (21)$$

Here, the laser intensity $I_\nu(\nu)$, the absorption cross-section $\sigma_{ik}(\nu)$, and the population difference $\Delta N(\nu)$, are all frequency-dependent. The frequency dependence of $\Delta N(\nu)$ is usually caused by the different thermal velocities resulting in different Doppler shifts.



For case $\Delta\nu_L \gg \delta\nu_a$, define the total laser intensity:

$$I = \int I_\nu(\nu)d\nu \approx I_\nu(\nu_0) \cdot \Delta\nu_L \qquad (22)$$

$$\Rightarrow I_\nu(\nu_0) \approx I/\Delta\nu_L.$$

Similarly, total absorption cross-section

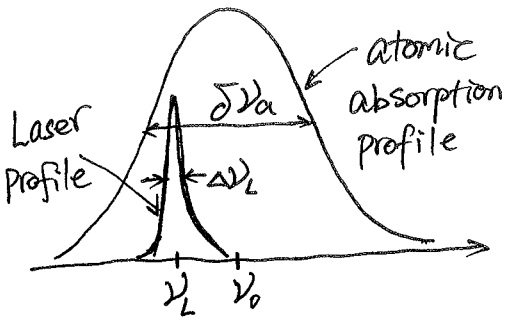
$$\sigma_{ik} = \int \sigma_{ik}(\nu)\, d\nu \approx \sigma_{ik}(\nu_0) \cdot \delta\nu_a \qquad (23)$$

$$\therefore dI = -dz \cdot \int I_\nu(\nu) \cdot \sigma_{ik}(\nu) \cdot \Delta N(\nu)\, d\nu$$

$$= -dz \cdot I_\nu(\nu_0) \cdot \sigma_{ik}(\nu_0) \cdot \delta\nu_a \cdot \Delta N$$

$$= -dz \cdot I \cdot \sigma_{ik}(\nu_0) \cdot \frac{\delta\nu_a}{\Delta\nu_L} \cdot \Delta N \qquad (24)$$

Here, the total absorption line is interacting with the laser, while only part of the laser ($I_L(\nu_0)$) interacts with the absorption line: $I_\nu(\nu_0) \approx I/\Delta\nu_L$, and it is relatively flat.



For case $\Delta\nu_L \ll \delta\nu_a$,
it usually goes by the integration form: $dI = -dz \cdot \int I_\nu(\nu)\, \sigma_{ik}(\nu)\, \Delta N(\nu)\, d\nu$. (25)

The absorption of the incident photons causes population changes of the levels involved in the absorbing transition. This can be described by the rate equations for the population densities N_1 and N_2 of the nondegenerate levels $|1\rangle$ and $|2\rangle$ with $g_1 = g_2 = 1$ (open 2-level system) ($\because B_{12} = B_{21}$)

$$\begin{cases} \dfrac{dN_1}{dt} = B_{12}\rho_\nu(N_2 - N_1) - R_1 N_1 + C_1 & (26) \\ \dfrac{dN_2}{dt} = B_{12}\rho_\nu(N_1 - N_2) - R_2 N_2 + C_2 & (27) \end{cases}$$

where $R_i N_i$ represents the total relaxation rate (including spontaneous emission) that depopulates the level $|i\rangle$,

$$C_i = \sum_k R_{ki} N_k + D_i \qquad (28)$$

takes care of all relaxation paths from the other levels $|k\rangle$ that contribute to the repopulation of the level $|i\rangle$, and also of the diffusion rate D_i of molecules in level $|i\rangle$ into the excitation volume.

Assume the quantities C_i are not noticeably changed by the radiation field. Under steady-state conditions $\frac{dN_1}{dt} = \frac{dN_2}{dt} = 0$, the unsaturated population difference ($\rho = 0$) is given by

$$\Delta N_0 = \Delta N(\rho=0) = N_1^\circ - N_2^\circ = \frac{C_1}{R_1} - \frac{C_2}{R_2} = \frac{C_1 R_2 - C_2 R_1}{R_1 R_2} \tag{29}$$

For saturated case,

$$\begin{cases} B_{12}\rho_\nu (N_2 - N_1) - R_1 N_1 + C_1 = B_{12}\rho_\nu (-\Delta N) - R_1 N_1 + C_1 = 0 \\ B_{12}\rho_\nu (N_1 - N_2) - R_2 N_2 + C_2 = B_{12}\rho_\nu (\Delta N) - R_2 N_2 + C_2 = 0 \end{cases}$$

$$\Rightarrow \begin{cases} N_1 = -\frac{B_{12}\rho_\nu}{R_1}\Delta N + \frac{C_1}{R_1} \\ N_2 = \frac{B_{12}\rho_\nu}{R_2}\Delta N + \frac{C_2}{R_2} \end{cases}$$

$$\therefore N_1 - N_2 = \frac{C_1}{R_1} - \frac{C_2}{R_2} - \Delta N \cdot B_{12}\rho_\nu \left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \Delta N$$

Recall $\frac{C_1}{R_1} - \frac{C_2}{R_2} = \Delta N_0$

$$\therefore \Delta N = \frac{\Delta N_0}{1 + B_{12}\rho_\nu \left(\frac{1}{R_1} + \frac{1}{R_2}\right)} \tag{30}$$

$$= \frac{\Delta N_0}{1+S}$$

where S is the saturation parameter

$$S = B_{12}\rho_\nu \left(\frac{1}{R_1} + \frac{1}{R_2}\right) = B_{12} I_\nu / (c \cdot R^*), \tag{31}$$

(c: light speed)

where $R^* = \frac{R_1 R_2}{R_1 + R_2}$ (i.e., $\frac{1}{R^*} = \frac{1}{R_1} + \frac{1}{R_2}$) (32)

S gives the ratio of the induced (stimulated) transition probability $B_{12}\rho_\nu$ to the "mean" relaxation probability R^*.

The intensity decrease of the incident laser from absorption along the length dz of the path is

$$dI = -dz \cdot I \cdot \sigma_{12}(\nu_0) \frac{\delta\nu_a}{\Delta\nu_L} \cdot \frac{\Delta N_0}{1+S} \qquad (33).$$

The intensity $I = I_s$ at which the saturation parameter $S=1$ is called the saturation intensity. From Eq. (31),

$$I_s = \frac{C \cdot R^*}{B_{12}} \qquad (34).$$

At the saturation intensity, the population density difference ΔN drops to half of its unsaturated value ΔN_0.

In case of incoherent light sources, such as spectral lamps, the intensity I_ν is so small that $S \ll 1$. Thus, Eq. (33) can be approximated by

$$dI = -dz \cdot I\,\sigma_{12} \cdot \Delta N_0 \cdot \frac{\delta\nu_a}{\Delta\nu_L} \qquad (35)$$

Since ΔN_0 is independent of I, the absorbed intensity is proportional to the incident intensity (linear absorption), i.e., dI/I is constant. Integration of Eq. (35) gives the Lambert – Beer law of linear absorption:

$$I = I_0\, e^{-\sigma_{12} \cdot \Delta N_0 \cdot z} = I_0 e^{-\alpha z} \qquad (36)$$

Note: Doppler broadening on absorption coefficient α_{ik}

Absorption Coefficient α_{ik}

Absorption cross-section σ_{ik}

Population number density N_i, N_k.

$$\alpha_{ik} = \sigma_{ik}\left(N_i - \frac{g_i}{g_k} N_k\right) \quad \text{for all cases}$$

$$\cong \sigma_{ik} \cdot N_i \quad \text{for weak light}$$

* In principle, σ_{ik} is the cross section for single atom/molecule, so $\sigma_{ik}(\omega)$ has a Lorentzian shape $\sigma_{ik}(\omega) = \sigma_0 L(\omega, v)$ where $L(\omega, v)$ is a Lorentzian shape and a function of velocity v. N_i is the population distribution along velocity, i.e., $N_i(v)$, which is Gaussian shape $N_i(v) = N_0 G(v)$ under Maxwellian distribution.

$$\therefore \alpha_{ik}(\omega) = \int_{-\infty}^{+\infty} \sigma_{ik}(\omega, v)\, N_i(v)\, dv$$

$$= \sigma_0 N_0 \int_{-\infty}^{+\infty} L(\omega, v)\, G(v)\, dv$$

Thus, $\alpha_{ik}(\omega)$ is a Voigt profile, i.e., the convolution of a Lorentzian with Gaussian.

* But it is common to shift all distribution factors to the absorption cross section, which is now a cross section for the molecule assembly (but normalized to single molecule), not for single molecule anymore. Then N_i will only

Count the total population.

* Therefore, it is more accurate to say

absorption / backscatter coefficient has Doppler broadening, instead of saying

absorption / backscatter cross section has Doppler broadening.

* In Doppler-free or Sub-Doppler spectroscopy, we have to use single atom/molecule absorption cross-section $\sigma_{ik}(\omega)$ that is Lorentzian with different velocity distributions of population to derive the sub-Doppler features.

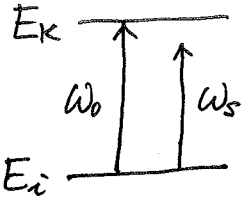
2. Saturation of Inhomogeneous Line Profiles

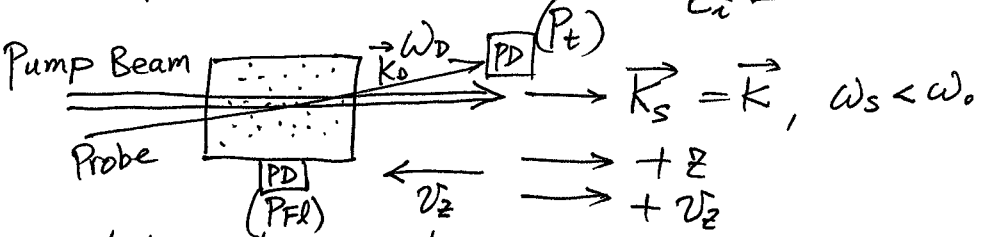
"Hole Burning & Lamp Dip"

From ground state population distribution $n_i(v_z)$

$\Rightarrow$ Transmitted power $P_t(\omega)$

$\Rightarrow$ Fluorescence power $P_{Fl}(\omega)$





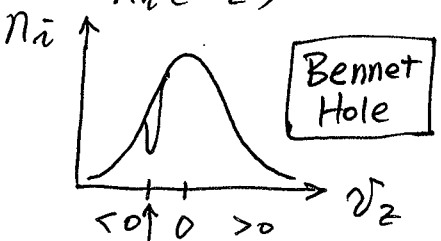
(1) Ground State population density distribution $n_i(v_z)$

① No pump beam : Gaussian Distribution

② Add pump beam : Burnt a hole

③ Where ? $\omega_L' = \omega_s - \vec{k}_s \cdot \vec{v} = \omega_0$

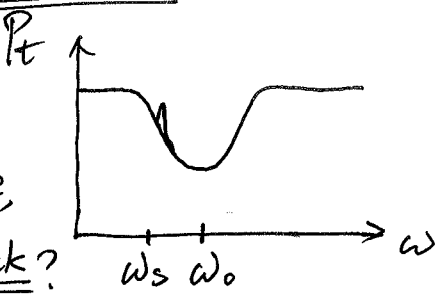
$\therefore \omega_s - k v_z = \omega_0 \Rightarrow \boxed{v_z = \frac{\omega_s - \omega_0}{k}} < 0$



(2) Transmitted probe beam Power $P_t(\omega)$

① No pump beam : Gaussian or Reversed Gaussian ?

② Add pump beam → burnt a hole in $n_i(v_z)$: When probe beam Scans through this distribution n_i hole, the transmitted beam has hole or peak ?



③ Where ? Depends on probe beam propagation direction If the same direction as pump beam, the saturated

Subgroup (of velocity) will see blue shift of the probe beam laser frequency:

$$\omega_D' = \omega_D - \vec{K}_D \cdot \vec{v}$$
$$= \omega_D - k v_z = \omega_0$$
$$\Rightarrow \omega_D = \omega_0 + k v_z$$

$\because k v_z < 0 \quad \therefore \omega_D < \omega_0$.

Substitute $v_z = \frac{\omega_s - \omega_0}{k}$ into above Equation:

$$\omega_D = \omega_0 + k \cdot \frac{\omega_s - \omega_0}{k} = \omega_s$$

(3) Fluorescence Power $P_{Fl}(\omega)$

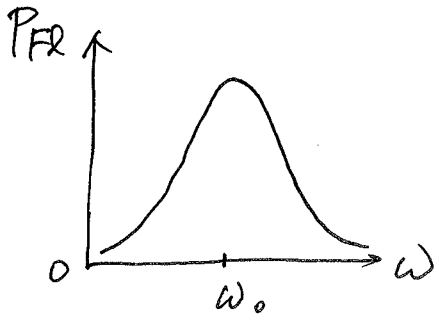
① No pump beam: Gaussian or Reversed Gaussian ?

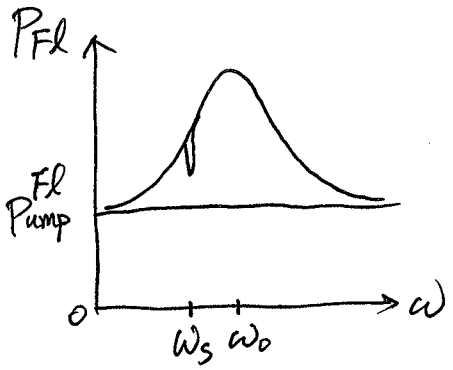
② Add pump beam: a constant fluorescence background occurs.

③ Fluorescence: peak or dip ?

④ where ? $\omega_D = \omega_s$

for same probe/pump propagation direction.



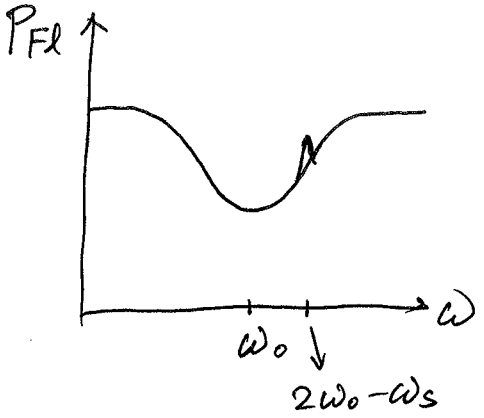


(4) If probe beam propagates in the opposite direction of the pump beam, pump beam produces the same hole on the ground state population distribution.

For transmitted power:

Gaussian or Reversed Gaussian ?

peak or dip ?



Where ? $\vec{K}_D = -\vec{K}_S = -\vec{K}$

$$\omega_D' = \omega_D - \vec{K}_D \cdot \vec{v}$$
$$= \omega_D - (-K) v_z = \omega_0$$

$$\Rightarrow \omega_D = \omega_0 - K v_z$$

$\because K v_z < 0 \quad \therefore \omega_D > \omega_0$

Substitute $v_z = \frac{\omega_s - \omega_0}{K}$ into above equation:

$$\omega_D = \omega_0 - K \cdot \frac{\omega_s - \omega_0}{K} = 2\omega_0 - \omega_s.$$

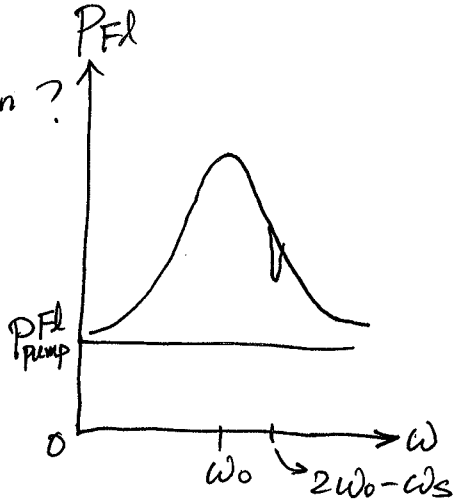
For fluorescence Power:

Gaussian or reversed Gaussian ?

Background added or not ?

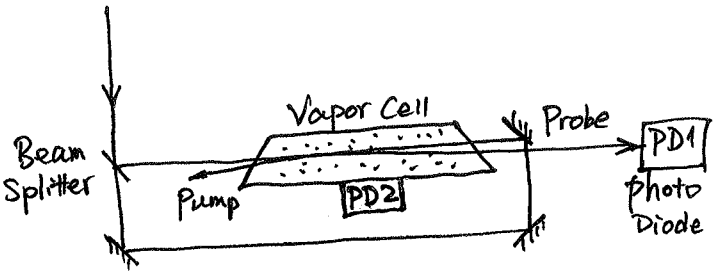
peak or dip ?

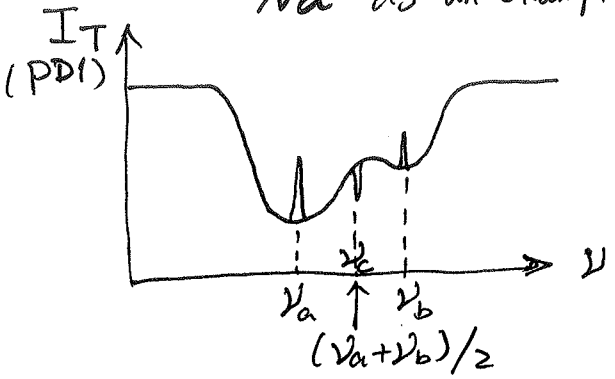
Where ?



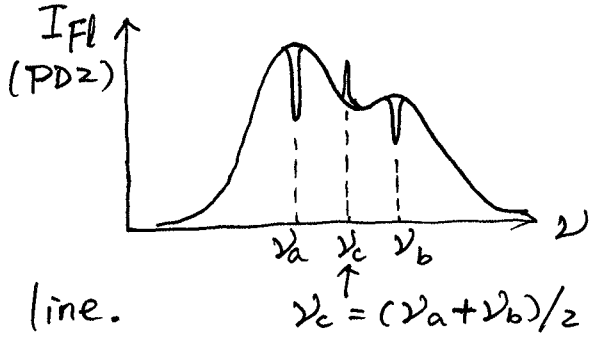
3. Saturation Spectroscopy:

Na as an example





For Na, K, Rb, Cs, the absorption is strong, resulting in direct saturation – absorption spectroscopy and saturation – fluorescence spectroscopy being strong enough for Doppler-free line.



When the absorption is weak or the fluorescence is weak, we can do intensity modulation by chopping the laser beam periodically with a chopper and then use lock-in amplifier to do phase sensitive detection to improve the detection sensitivity:

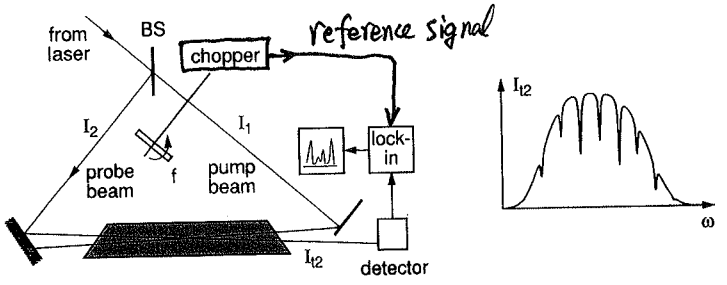
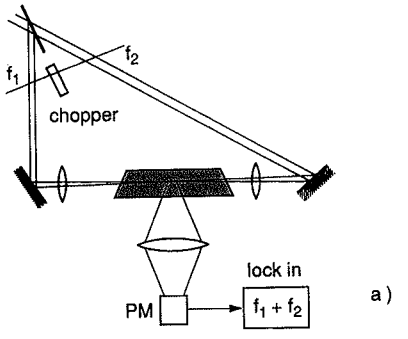


Fig. 7.9. Experimental setup for saturation spectroscopy where the transmitted probe intensity $I_2(\omega)$ is monitored

Strong Beam Saturates and Weak Beam Probes from the opposite direction.



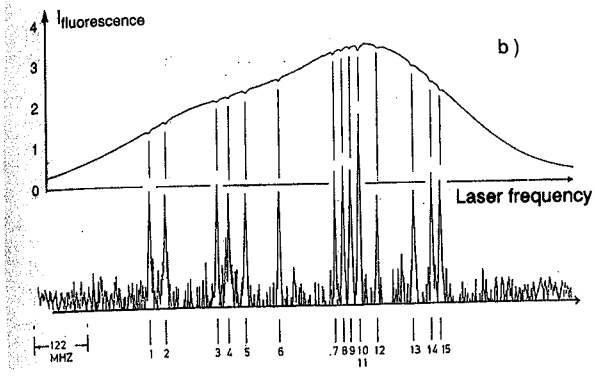


Fig. 7.12a,b. Intermodulated fluorescence method for saturation spectroscopy at small densities of the sample molecules: (**a**) experimental arrangement; (**b**) hyperfine spectrum of the $(v''=1, J''=98) \rightarrow (v'=58, J'=99)$ line in the $X^1\Sigma_g \rightarrow {}^3\Pi_{ou}$ system of I_2 at $\lambda = 514.5\,\text{nm}$, monitored at the chopping frequency f_1 of the pump beam (*upper spectrum* with the Lamb dips) and at $(f_1 + f_2)$ (*lower spectrum*) [7.10]

4. Polarization Spectroscopy

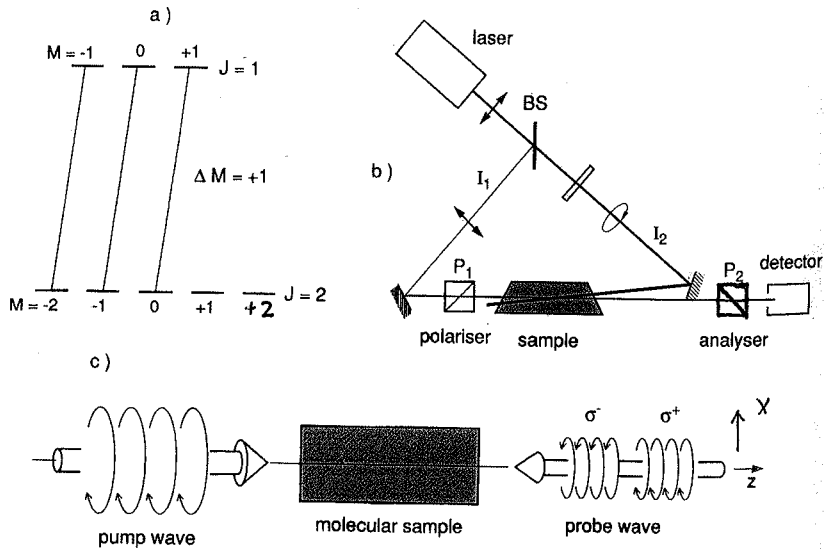
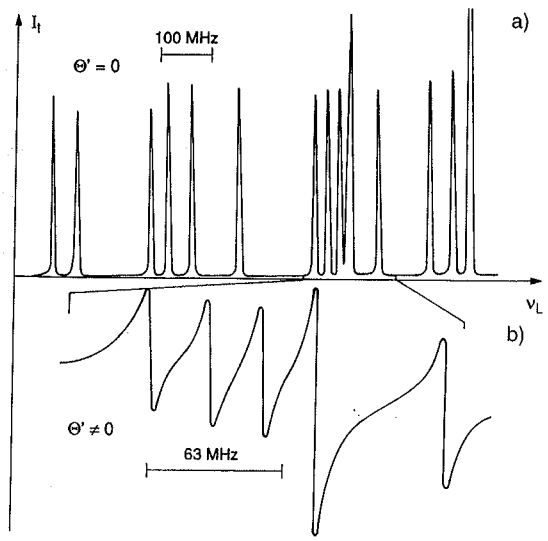


Fig. 7.20a–c. Polarization spectroscopy: (**a**) level scheme for a P transition $J = 2 \rightarrow J = 1$; (**b**) experimental setup; (**c**) linearly polarized probe wave as superposition of σ^+ (angular momentum +5 in z-direction) and σ^- components

The signals from polarization Spectroscopy come mainly from the change of the polarization state of the probe wave induced by a polarized pump wave. Because of optical pumping, the pump wave causes a change of refractive index n and absorption coefficient α.



absorption

dispersion

Fig. 7.22a,b. Polarization spectrum of the same hyperfine components of I_2 as shown in Fig. 7.12 with circularly polarized pump: (**a**) with $\theta' = 0$; (**b**) with $\theta' \neq 0$

Linear Polarization $\rightarrow \sigma^+ + \sigma^-$

Selective polarized pumping $\rightarrow$

$\Delta\alpha = \alpha^+ - \alpha^-$

$\Delta n = n^+ - n^-$

i.e., Anisotropic Sample becomes birefringent

$\Rightarrow$ rotation of polarization

$\Rightarrow$ Some rotated polarization light can pass the crossed polarizer P_2. Only when $\omega = \omega_0$, the pump and probe beams interact with the same sub-group of velocity $\longrightarrow$ sub-Doppler feature !

§15.2. Two-Photon Spectroscopy and Molecular Beam Spectroscopy

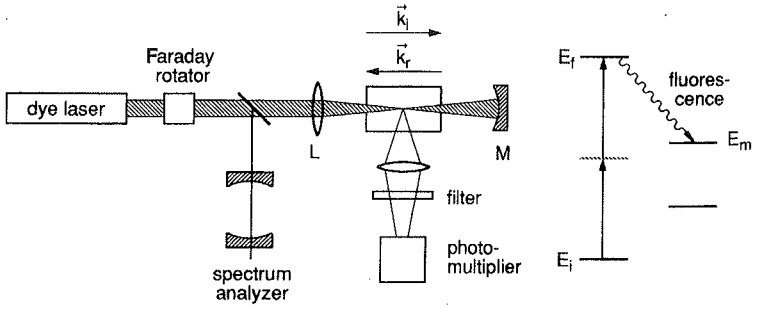


Fig. 7.28. Experimental arrangement for Doppler-free two-photon spectroscopy

The resonance condition for the simultaneous absorption of two photons is

$$(E_f - E_i)/\hbar = (\omega_1' + \omega_2') = \omega_1 + \omega_2 - \vec{v}\cdot(\vec{k}_1 + \vec{k}_2)$$

If two photon absorbed are from two light waves with $\omega_1 = \omega_2 = \omega$ but $\vec{k}_1 = -\vec{k}_2$, the $(\omega_1' + \omega_2') = \omega_1 + \omega_2$, i.e., the Doppler shift of the two-photon transition becomes zero. This means that all molecules, independent of their velocities, absorbs at the same sum frequency $\omega_1 + \omega_2 = 2\omega$.

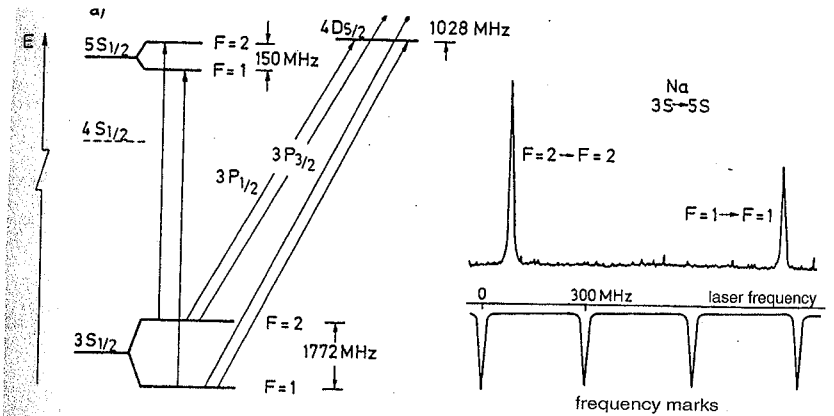


Fig. 7.29a,b. Doppler-free two-photon spectrum of the 3S → 5S and 3S → 4D transitions in the Na atom: (**a**) level scheme; (**b**) 3S → 5S transition with resolved hyperfine structure [7.43]

Although the probability of a two-photon transition is generally much lower than that of a single-photon transition, the fact that all molecules in the absorbing state can contribute to the signal may outweigh the lower transition probability, and the signal amplitude may even become, in favorable cases, larger than that of the saturation signals.

Molecular Beam Spectroscopy: to largely reduce 1st-order Doppler shift $\vec{k}\cdot\vec{v}$ when $\vec{k}$ is perpendicular to molecular beam velocity $\vec{v}$.

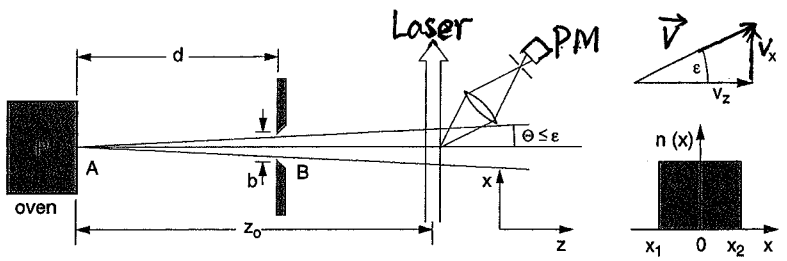


Fig. 9.1a,b. Laser excitation spectroscopy with reduced Doppler width in a collimated molecular beam: (**a**) schematic experimental arrangement; (**b**) collimation ratio and density profile $n(x)$ in a collimated beam effusing from a point source A

§15.3. Ramsey Fringes : Ramsey's idea of separated field

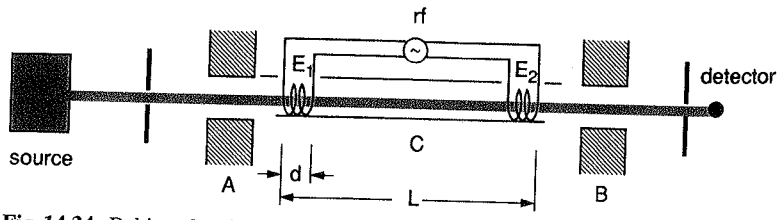


Fig. 14.34. Rabi molecular beam apparatus with Ramsey's separated fields

Ramsey won Nobel prize in 1989 for his contribution of the Separated Oscillation fields and H-masers.

Original Ramsey fringes are in rf domain.

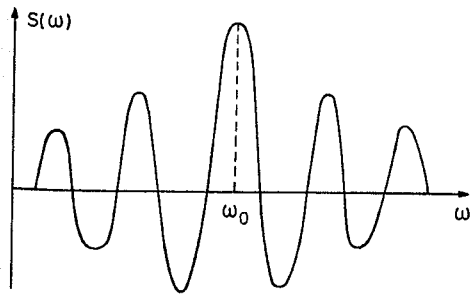


Fig. 14.35. Signal power absorbed by the molecules in the second field as a function of detuning $\Omega = \omega - \omega_0$ (Ramsey fringes) for a narrow velocity distribution $N(v)$

Molecular beam spectroscopy largely removes the Doppler broadening caused by the 1st order Doppler shift. However, molecular beam suffers transit-time broadening due to limited interaction time with the radiation field.

Norman Ramsey's separated oscillation field idea (Fig. 14.34) dramatically reduces the time-of-flight broadening and enables the Cs atomic beam clock to be the primary clock in 1980s.

The atoms in the beam pass two phase-coherent fields that are spatially separated by the distance $L >> d$ (d is the extension of each field). The result is similar to Young's interference with partially coherent light, and the transit-time width is reduced to $\sim v/L$. Since $L >> d$, the central fringe of the interference pattern (figure 14.35) is much narrower than the original spectral line.