DSFTA

Doppler broadening free spectroscopy

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Overview

1. Introduction to the spectral linewidth
2. Doppler-free spectroscopy
3. Doppler-free spectroscopy at ISOLDE-RILIS
4. Conclusions

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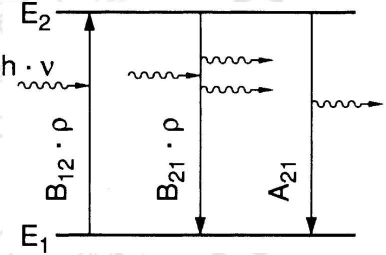
Absorption, Induced, and Spontaneous Emission



- probability per second that a molecule absorbs one photon [1]

$$\frac{d}{dt}\mathcal{P}_{12} = B_{12}\rho(\nu) \tag{1}$$

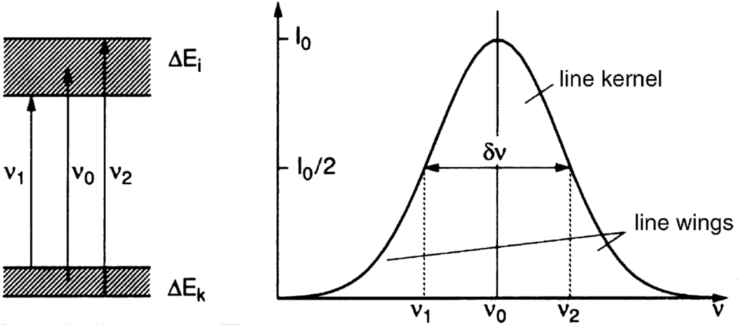
- probability per second that a molecule emits one induced photon

$$\frac{d}{dt}\mathcal{P}_{21} = B_{21}\rho(\nu) \tag{2}$$

- probability per second that a molecule emits spontaneously one photon

$$\frac{d}{dt}\mathcal{P}_{21}^{\mathrm{spont}} = A_{21} \tag{3}$$

Line profile



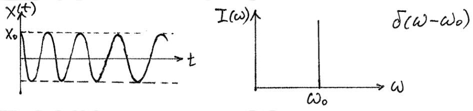
- The energy levels have a finite width due to the energy–time uncertainty principle
- The function $I(\nu)$ in the vicinity of ν_0 is called the *line profile*

$$\nu_0 = \frac{E_i - E_k}{h} \tag{4}$$

$\delta\nu$ is the FWHM of the line

Natural Linewidth

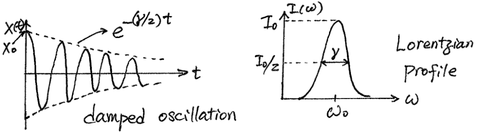
harmonic oscillator



$$\ddot{x} + \omega_0^2 x = 0 \tag{5}$$

$$x(t) = x_0 \cos \omega_0 t \tag{6}$$

damped harmonic oscillator



$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = 0 \tag{7}$$

$$x(t) = x_0 e^{-\frac{\gamma}{2} t} [\cos \omega t + \frac{\gamma}{2\omega} \sin \omega t] \tag{8}$$

$$\omega = \sqrt{\omega_0^2 - \frac{\gamma^2}{4}} \xrightarrow{\gamma \ll \omega_0} \omega_0 \tag{9}$$

$$x(t) = x_0 e^{-\frac{\gamma}{2} t} \cos \omega_0 t \tag{10}$$

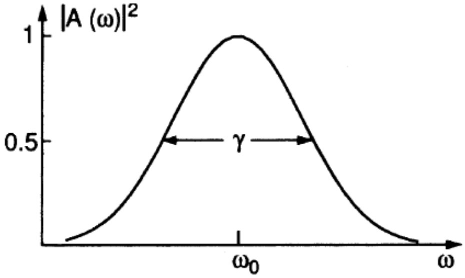
- atoms modeled as damped harmonic oscillators with central frequency $\omega_0 = 2\pi\nu_0$ that corresponds to $\omega_{ik} = \frac{E_i - E_k}{\hbar}$

Lorentzian line profile

- damped oscillation as superposition of monochromatic oscillations

$$x(t) = \frac{1}{2\sqrt{2\pi}} \int_0^\infty A(\omega) e^{i\omega t} d\omega \qquad (11)$$

- amplitude $A(\omega)$ as Fourier transform



- real intensity is $I(\omega) \propto A(\omega)A^*(\omega)$

$$I(\omega - \omega_0) = \frac{C}{(\omega - \omega_0)^2 + (\gamma/2)^2} \qquad (12)$$

- normalized intensity

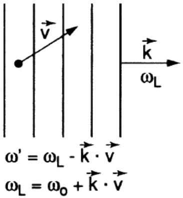
$$L(\omega - \omega_0) = \frac{\gamma/2\pi}{(\omega - \omega 0)^2 + (\gamma/2)^2} \qquad (13)$$

with FWHM $= \gamma$

Broadening of the natural linewidth

- Saturation broadening
- Power broadening
- Collisional broadening
- Transit-Time Broadening
- **Doppler broadening**

Linear Doppler shift



- In first approximation there is a linear relation between the particle velocity and the frequency shift with respect to an energy level gap $\hbar\omega_0$
- excited molecule with velocity $\boldsymbol{v} = v_x, v_y, v_z$ emits

$$\omega_{\rm e} = \omega_0 + \boldsymbol{k} \cdot \boldsymbol{v} \tag{14}$$

- excitable molecule with velocity $\boldsymbol{v} = v_x, v_y, v_z$ absorbs

$$\omega_{\rm a} = \omega_0 + \boldsymbol{k} \cdot \boldsymbol{v} \tag{15}$$

Doppler Width

- At thermal equilibrium, the molecules of a gas follow a Maxwellian velocity distribution
- Intensity profile for such distribution with central frequency ω_0 is a Gaussian distribution

$$I(\omega) = I_0 \exp\left[-\left(\frac{c(\omega - \omega_0)}{\omega_0 v_p}\right)^2\right] \tag{16}$$

with most probable velocity $v_{\mathrm{p}} = \sqrt{\frac{2kT}{m}}$

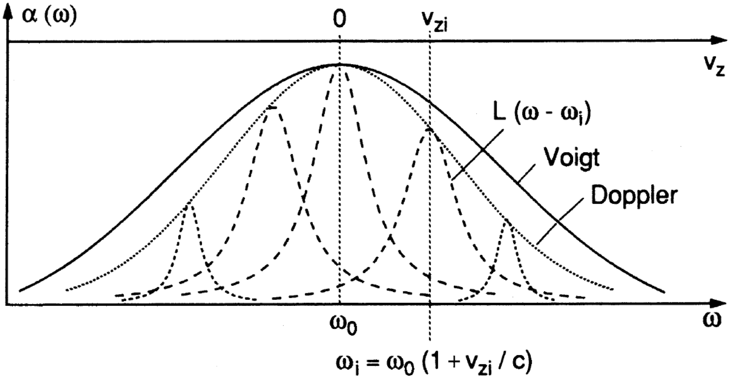
- Doppler width $\delta\omega_{\mathrm{D}}$ is the FWHM of such Gaussian profile

$$\delta\omega_{\mathrm{D}} = \frac{\omega_0}{c}\sqrt{\frac{8kT\ln 2}{m}} \propto \omega_0\sqrt{\frac{T}{m}} \tag{17}$$

Voigt Profile

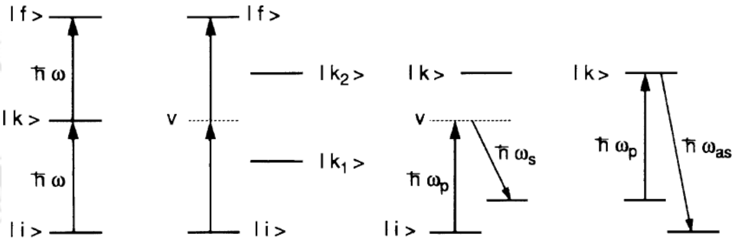
- convolution between Gaussian and Lorentzian

$$I(\omega) = C \int_0^\infty \frac{\exp\left(-\left(\frac{c}{v_p}\frac{\omega_0-\omega'}{\omega_0}\right)^2\right)}{(\omega-\omega')^2+(\gamma/2)^2} d\omega' \qquad \text{with} \qquad C = \frac{\gamma N_i c}{2 v_\mathrm{p} \pi^{3/2} \omega_0} \tag{18}$$



Overview

Two-photon absorption



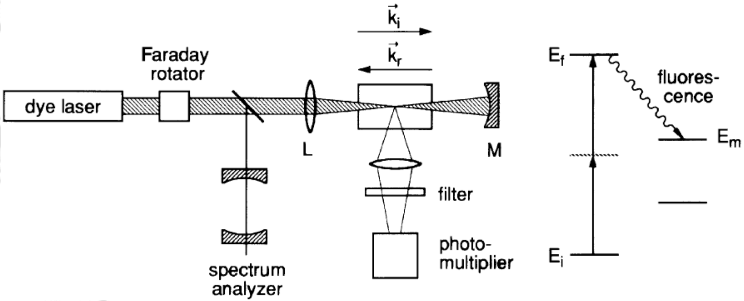
- Theory from Maria Goeppert-Mayer in 1929 [2]
- Transition $E_i \to E_f$ given by several photons of energy ω_i such that $E_f - E_i = \hbar \sum_i \omega_i$

$$A_{if} \propto \frac{\gamma_{if} I_1 I_2}{[\omega_{if} - \omega_1 - \omega_2 - \boldsymbol{v} \cdot (\boldsymbol{k}_1 + \boldsymbol{k}_2)]^2 + (\gamma_{if}/2)^2} \times \text{another factor} \qquad (19)$$

- For $\boldsymbol{k}_1 = -\boldsymbol{k}_2$ the Doppler broadening vanishes

$$A_{if} \propto \frac{\gamma_{if} I_1 I_2}{[\omega_{if} - \omega_1 - \omega_2]^2 + (\gamma_{if}/2)^2} \times \text{another factor} \qquad (20)$$

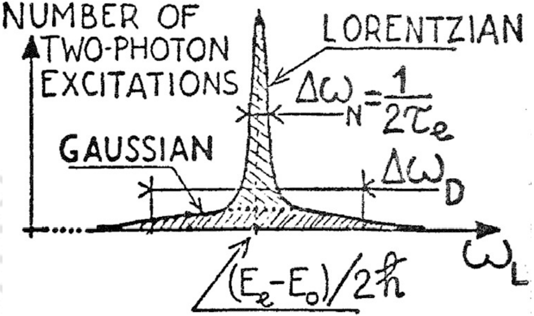
Doppler-free multiphoton spectroscopy



- Using two photons out of the same laser is disadvantageous

$$2\omega = \frac{E_f - E_i}{\hbar} \tag{21}$$

Two-photon spectrum

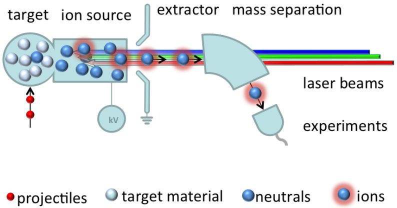


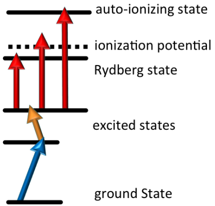
- The spectrum contains two contributions according to the origin of the two photons:
  - Doppler-broadened Gaussian $\leftarrow$ photons from the same beam
  - Doppler-free Lorentzian $\leftarrow$ photons from counter-propagating beams
- The Gaussian background can be eliminated using polarized beams

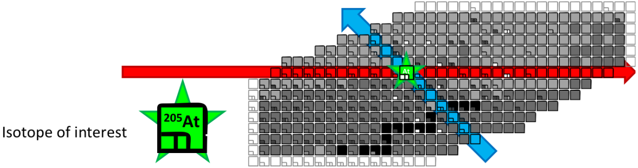
Overview

ISOLDE at CERN

ISOLDE-RILIS

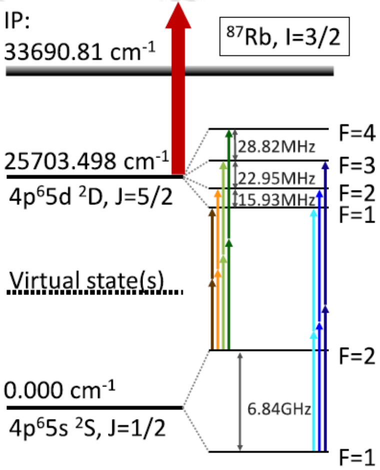






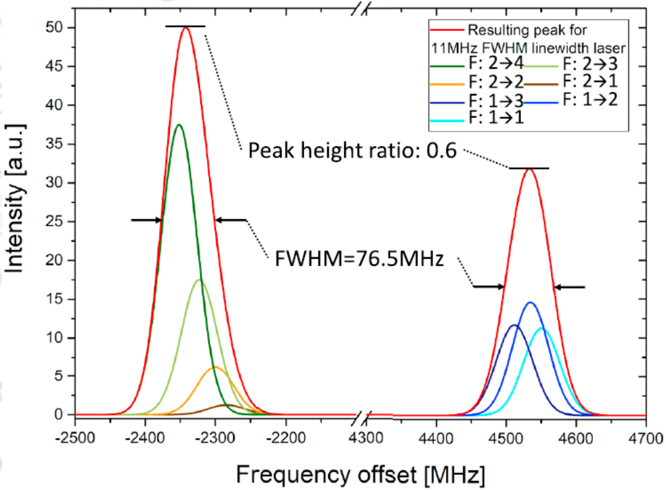
- Radioactive species are produced in a thick target during its bombardment by proton beam (ISOL technique)
- Multiple laser beams with specific wavelengths are used to match a series of successive electronic transition energies, unique to that element [3]

Introduction to the experiment



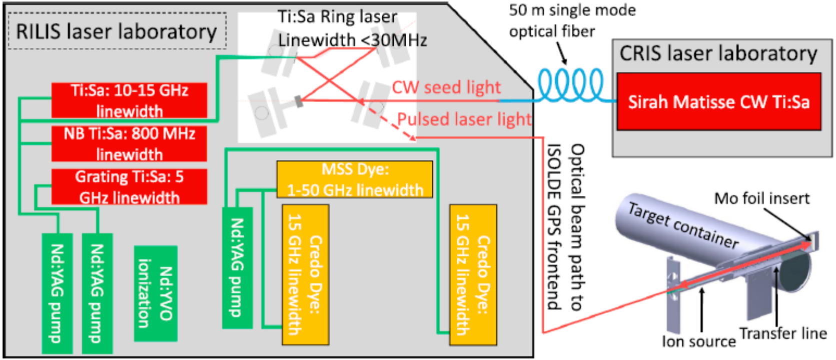
- Laser ionization scheme for rubidium
- The hyperfine structure is depicted along with the corresponding shifts (not to scale) and the possible 2-photon transitions
- The goal of this work is to measure the Doppler-free linewidth, in order to determine the feasibility of laser linewidth limited high-resolution in-source spectroscopy
- At 2000 K the Doppler broadening is 2.2 GHz for stable rubidium isotopes
- The frequency of the spectra is given relative to the transition centroid at 25703.498 cm^{-1}

Simulated Spectrum



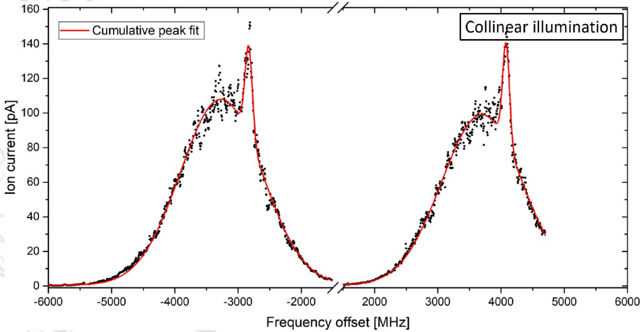
- The individual transitions can not be resolved under the experimental conditions
- The 6.84 GHz split of the ground level can be resolved
- Assumed laser linewidth $\sim 10\,\mathrm{MHz}$

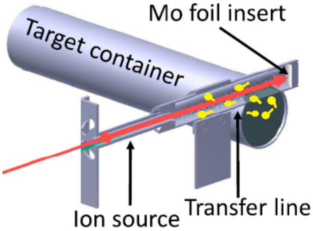
Collinear Doppler-free 2-photon resonance ionization



- First demonstration of Doppler-free 2-photon in-source laser spectroscopy at the ISOLDE-RILIS [4]
- Mirror realized with a flat molybdenum foil

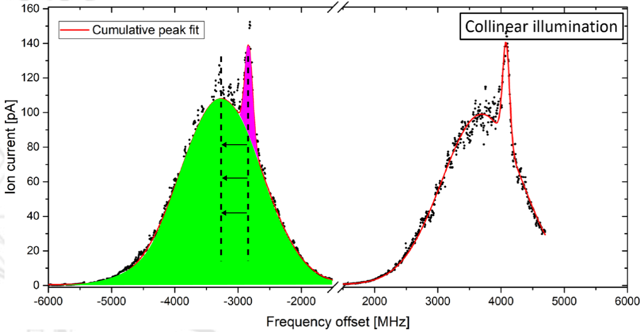
ISOLDE two-photons results

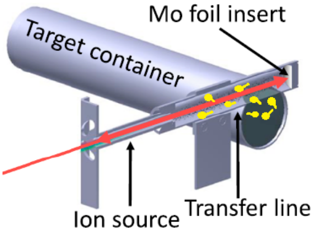




- narrow Doppler-free signal
- Doppler broadened and shifted background:
  - the atom source, transfer line and ion source geometry results in an atomic sample with predominantly velocity components towards the extraction electrode
  - the reflectivity is less than 100 %

ISOLDE two-photons results





- narrow Doppler-free signal
- Doppler broadened and shifted background:
  - the atom source, transfer line and ion source geometry results in an atomic sample with predominantly velocity components towards the extraction electrode
  - the reflectivity is less than 100 %

Conclusions

- Doppler broadening is a major limitation in laser spectroscopy
- Doppler-free spectroscopy can be achieved through two-photon absorption
- At CERN-ISOLDE this technique was used to measure the spectral profiles of rubidium atoms

Thank you for the attention

References I

[1] Wolfgang Demtröder. "Absorption and Emission of Light". In: *Laser Spectroscopy 1: Basic Principles*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2014, pp. 5–74. ISBN: 978-3-642-53859-9. DOI: 10.1007/978-3-642-53859-9_2. URL: https://doi.org/10.1007/978-3-642-53859-9_2.

[2] Wolfgang Demtröder. *Laser Spectroscopy 2: Experimental Techniques*. Springer Berlin Heidelberg, 2015. Chap. 2, pp. 118–131. ISBN: 9783662446416. DOI: 10.1007/978-3-662-44641-6. URL: http://dx.doi.org/10.1007/978-3-662-44641-6.

[3] URL: https://rilis-web.web.cern.ch/ (visited on 11/25/2024).

References II

[4] K. Chrysalidis et al. "First demonstration of Doppler-free 2-photon in-source laser spectroscopy at the ISOLDE-RILIS". In: *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 463 (2020), pp. 476–481. ISSN: 0168-583X. DOI: doi.org/10.1016/j.nimb.2019.04.020. URL: https://www.sciencedirect.com/science/article/pii/S0168583X19302046

[5] Peter W. Milonni and Joseph H. Eberly. "Laser Oscillation: Gain and Threshold". In: *Laser Physics*. John Wiley & Sons, Ltd, 2010. Chap. 4, pp. 141–173. ISBN: 9780470409718. DOI: https://doi.org/10.1002/9780470409718.ch4. eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/9780470409718.ch4. URL: https://onlinelibrary.wiley.com/doi/abs/10.1002/9780470409718.ch4.

References III

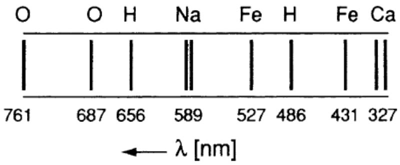
[6] Peter W. Milonni and Joseph H. Eberly. “Laser Oscillation: Power and Frequency”. In: *Laser Physics*. John Wiley & Sons, Ltd, 2010. Chap. 5, pp. 175–228. ISBN: 9780470409718. DOI: https://doi.org/10.1002/9780470409718.ch5. eprint: https://onlinelibrary.wiley.com/doi/pdf/10.1002/9780470409718.ch5. URL: https://onlinelibrary.wiley.com/doi/abs/10.1002/9780470409718.ch5.

Back-up

Questions

- How long is a laser pulse?
- Is it possible to have no crossing of the forward and back propagating beams in the source
- What is the maximum time interval to have two-photon absorption and not one photon absorbed after the other?

Spectroscopy



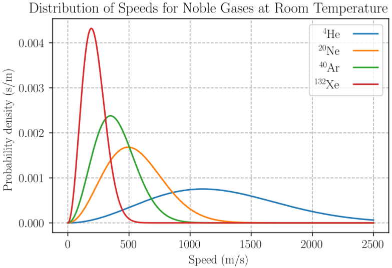
Fraunhofer lines in the spectrum of the sun

Spectroscopy

- Spectroscopic investigations allow us to study atoms and molecules structures [1]

Maxwell-Boltzmann distribution

- this implies that the momenta p and kinetic energies E_{kin} of the various particle species follow a Maxwell-Boltzmann distribution



Maxwell-Boltzmann equations

$$n(p)dp = \sqrt{2}\pi N\left(\frac{1}{\pi m K_B T}\right)^{3/2} p^2 e^{-\frac{p^2}{2mK_BT}}\,dp \tag{22}$$

where N denotes the total number of particles in the system and m their mass

Cavity Modes

assumptions [1]

- cubic cavity with the sides L at the temperature T
- walls of the cavity absorb and emit electromagnetic radiation
- at thermal equilibrium $\implies P_{\mathrm{a}}(\omega) = P_{\mathrm{e}}(\omega) \quad \forall\omega$

stationary radiation field $\boldsymbol{E}$

$$\boldsymbol{E} = \sum_p \boldsymbol{A}_p \exp[\mathrm{i}(\omega_p t - \boldsymbol{k}_p \cdot \boldsymbol{r}] + \text{c.c.} \tag{23}$$

Thermal Radiation and Planck's Law

Rayleigh-Jeans law

- classical oscillators applied to the cubic cavity

$$\rho(\nu)d\nu = n(\nu)kTd\nu = \frac{8\pi\nu^2 k}{c^3}Td\nu \tag{24}$$

Planck's radiation law

- only discrete amounts $qh\nu$ with q integer can be absorbed/emitted by the radiation field

$$\rho(\nu)d\nu = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{h\nu/kT}-1}d\nu \tag{25}$$

Spectroscopy Instrumentation

- the nuclear time scale is

$$\tau_n = \frac{E_n}{L} F \tag{26}$$

where E_n is the nuclear energy reservoir, L is the luminosity and F the fraction of reservoir available

Power Broadening

- Fermi-Dirac distribution must be used

$$n(p)dp = \frac{8\pi p^2}{h^3}\left(\frac{1}{1+e^{-\eta+E\mathrm{kin}/K_B T}}\right)dp \tag{27}$$

- in the case of electron degeneracy the electron pressure does not depend on the temperature

$$P = 1.0036 \times 10^{13}\left(\frac{\rho}{\mu_e}\right)^{5/3} \tag{28}$$

Other sources of spectral line broadening

- collisional broadening
- power broadening

Quadratic Doppler shift

The momentum $\boldsymbol{p}_i$ of an atom absorbing a photon with momentum $\hbar\boldsymbol{k}$ and energy $\hbar\omega_{ik} \simeq E_k - E_i$ changes to

$$\boldsymbol{p}_k = \boldsymbol{p}_i + \hbar\boldsymbol{k} \tag{29}$$

Using relativistic energy considerations:

$$\hbar\omega_{ik} = \sqrt{p_k^2 + (M_0c^2 + E_k)^2} - \sqrt{p_i^2c^2 + (M_0c^2 + E_i)^2} \tag{30}$$

Use Taylor expansion:

$$\omega_{ik} = \underbrace{\omega_0}_{\text{at rest}} + \underbrace{\boldsymbol{k}\cdot\boldsymbol{v}_i}_{\text{linear Doppler}} \underbrace{-\omega_0\frac{v_i^2}{2c^2} + \frac{\hbar\omega_0^2}{2Mc^2}}_{\text{quadratic Doppler} \to \text{recoil}} + \dots \tag{31}$$

cross section

$$\text{stimulated emission rate} = \sigma(\nu)\frac{\text{number of incident photons}}{\text{area} \cdot \text{time}} \tag{32}$$

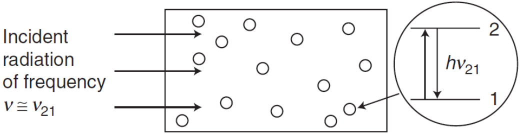
with

$$\sigma(\nu) = \frac{\lambda^2 A_{21}}{8\pi} S(\nu) \tag{33}$$

it depends on:

- spontaneous emission rate A_{21}
- lineshape function $S(\nu)$
- transition wavelength λ

Lasing



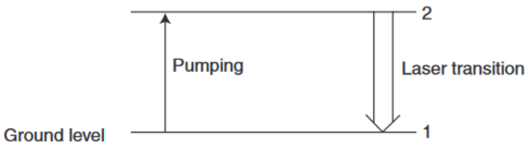
Suppose a beam of photons of energy $h\nu_{21}$ passing through a medium:

- $N_2 < N_1 \rightarrow$ absorption $\rightarrow g < 0$
- $N_2 > N_1 \rightarrow$ amplification $\rightarrow g > 0$

Having defined the gain coefficient g as

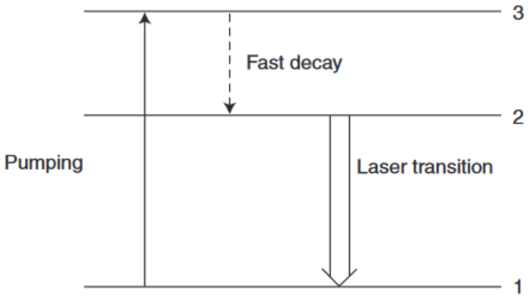
$$g(\nu) = \sigma(\nu)\left(N_2 - \frac{g_2}{g_1}N_1\right)I_\nu \tag{34}$$

Two-level scheme



- Just two levels do not allow for population inversion
- The pump will also contribute to the depletion of the higher level

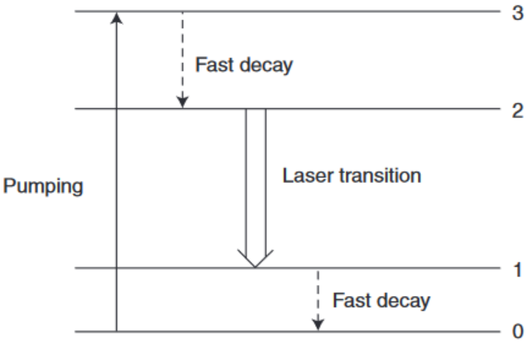
Three-level scheme



- Population inversion is possible having decoupled the pump from the laser transition

$$\bar{N}_2 - \bar{N}_1 = \frac{P - \Gamma_{21}}{P + \Gamma_{21}} N \tag{35}$$

Four-level scheme



- Population inversion is guaranteed ($\bar{N}_2 - \bar{N}_1 > 0$ always) choosing a medium with spontaneous emission coefficients such that $\Gamma_{10} > \Gamma_{21}$

$$\bar{N}_2 - \bar{N}_1 = \frac{\Gamma_{10} - \Gamma_{21}}{\Gamma_{10}\Gamma_{21} + P\Gamma_{21} + P\Gamma_{10}} PN \xrightarrow{\Gamma_{10} \gg \Gamma_{21}, P} \frac{P}{P + \Gamma_{21}} N \tag{36}$$

Equations ruling the states' populations

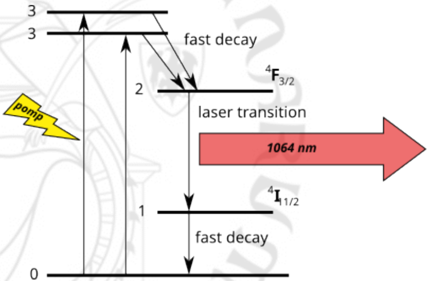
$$\frac{dN_0}{dt} = -PN_0 + \Gamma_{10} N_1 \tag{37}$$

$$\frac{dN_1}{dt} = -\Gamma_{10} N_1 + \Gamma_{12} N_2 + \sigma(\nu)(N_2 - N_1)\Phi_\nu \tag{38}$$

$$\frac{dN_2}{dt} = PN_0 - \Gamma_{21} N_2 - \sigma(\nu)(N_2 - N_1)\Phi_\nu \tag{39}$$

assuming that the decay $3 \rightarrow 2$ is much faster than the others so that $N_3 \approx 0$

Nd:YAG



- Neodymium-doped Yttrium Aluminum Garnet $\rightarrow$ $Nd{:}Y_3Al_5O_{12}$
- Neodymium impurities are in a +3 oxidation state (Nd(III))
- Nd(III) typically replace about 1 % of the Y atoms in the crystal structure of the YAG
- Nd:YAG laser is approximately a four-level system

Saturation

- Assume a two-level system with no pump
- The steady state solutions for the number of atoms in the two energy levels are

$$\bar{N}_2 = \frac{\frac{1}{2} I_\nu / I_\nu^{\mathrm{sat}}}{1 + I_\nu / I_\nu^{\mathrm{sat}}} N \tag{40}$$

$$\bar{N}_1 = \frac{1 + \frac{1}{2} I_\nu / I_\nu^{\mathrm{sat}}}{1 + I_\nu / I_\nu^{\mathrm{sat}}} N \tag{41}$$

- I_ν is the intensity of the photons with energy $h\nu$ in the medium
- I_ν is not related to the pump intensity, that is not considered here
- the saturation intensity

$$I_\nu^{\mathrm{sat}} = \frac{h\nu A_{21}}{2\sigma(\nu)} \tag{42}$$

provides the measure of whether a given field intensity I_ν is large or small in terms of its ability to saturate the transition $1 \rightarrow 2$

Saturation

The absorption coefficient is

$$a(\nu) = \sigma(\nu)(\bar{N}_1 - \bar{N}_2) = \frac{\sigma(\nu)N}{1 + I_\nu / I_\nu^{\mathrm{sat}}} \equiv \frac{a_0(\nu)}{1 + I_\nu / I_\nu^{\mathrm{sat}}} \tag{43}$$

- $I_\nu \ll I_\nu^{\mathrm{sat}} \rightarrow \quad \bar{N}_1 \approx N, \quad \bar{N}_2 \approx 0, \quad a(\nu) \approx a_0(\nu)$
- $I_\nu \gg I_\nu^{\mathrm{sat}} \rightarrow \quad \bar{N}_1 \approx N/2, \quad \bar{N}_2 \approx N/2, \quad a(\nu) \approx 0$
- as I_ν grows the stimulated absorption and emission processes overshadow the spontaneous emission ones

Power broadening

- Consider a homogeneously broadened transition having a Lorentzian lineshape of width $\delta\nu_0$

$$a(\nu) = \frac{a_0(\nu_0)\delta\nu_0^2}{(\nu-\nu_0)^2 + \delta\nu_0'^2} \tag{44}$$

with

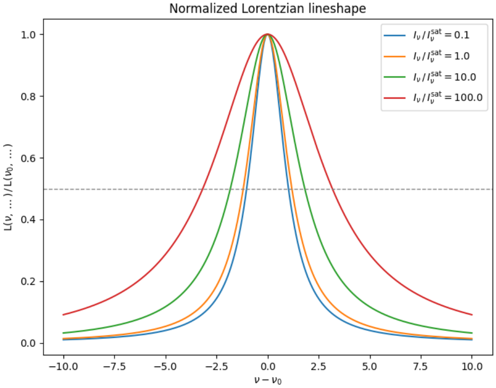
$$\delta\nu_0' = \delta\nu_0\sqrt{1 + I_\nu / I_\nu^{\mathrm{sat}}} \tag{45}$$

and

$$a_0(\nu_0) = \frac{\lambda^2 A_{21} N}{8\pi^2 \delta\nu_0} \tag{46}$$

- We can interpret the saturation of the transition with increasing intensity as an effective power broadening of the linewidth

Power broadening



- In general the saturation intensity I_ν^{sat} will depend on both upper- and lower-level decay rates associated with collisional as well as radiative processes, and it can also depend on the level degeneracies
- what matters is that absorption $a(\nu)$ and gain $g(\nu)$ coefficients saturates increasing the intensity as $\sqrt{1 + I_\nu / I_\nu^{sat}}$, whatever the form of I_ν^{sat}

Saturation for a four-levels scheme

- We consider a four-level scheme with pumping rate P
- Gain coefficient

$$g(\nu) = \frac{g_0(\nu)}{1 + I_\nu / I_\nu^{sat}} \tag{47}$$

- saturation intensity

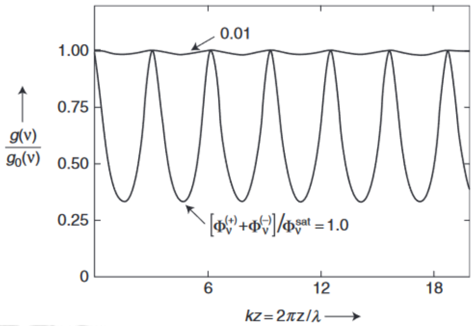
$$I_\nu^{sat} = h\nu\Phi_\nu^{sat} \tag{48}$$

- saturation flux

$$\Phi_\nu^{sat} = \frac{P + \Gamma_{21}}{\sigma(\nu)} \tag{49}$$

the saturation coefficients depends also on the pumping rate P

Spatial Hole Burning

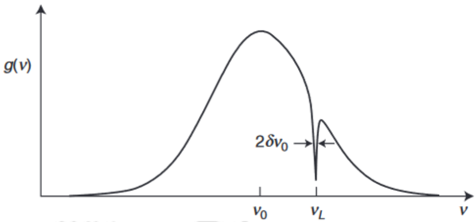


- In most lasers there is a standing wave rather than a traveling one

$$\Phi_\nu = \Phi_\nu^{(+)} + \Phi_\nu^{(-)} \qquad (50)$$

- Therefore, the intensity of the field I_ν is affected by the interference of the two oppositely propagating waves
- The gain $g(\nu)$ has a term $sin^2 kz$ that modulates its maximum, small signal value $g_0(\nu)$ along the cavity $\rightarrow$ spatial hole burning

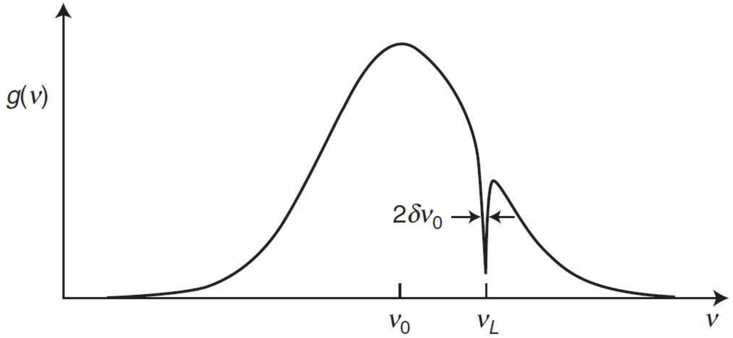
Spectral Hole Burning



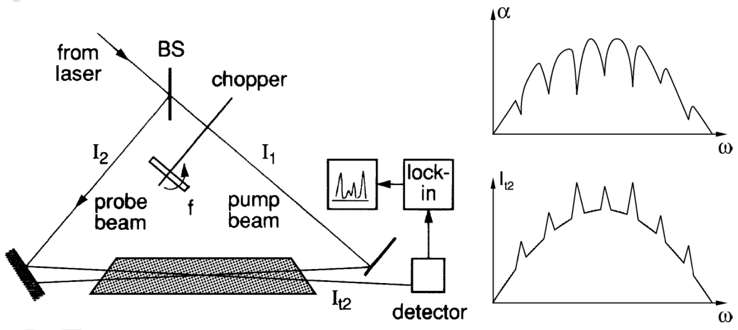
- Consider an inhomogeneously broadened medium where the atoms have different central transition frequencies ν_0'
- The cavity mode frequency is ν
- The absorption or gain is more strongly saturated for spectral packets with frequency $\nu_0' \approx \nu_0$
- The selective saturation leads to spectral hole burning in the gain curve

Hole burning

- Spectral hole burning is the origin of the Lamb dip in Doppler-broadened lasers [5]
- This dip in output power at line center was predicted by W. E. Lamb, Jr. in 1963, and is called the Lamb dip [6]

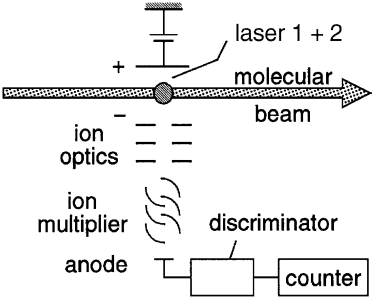


Saturation spectroscopy



- https://www.youtube.com/watch?v=hY21ndCeZ9I

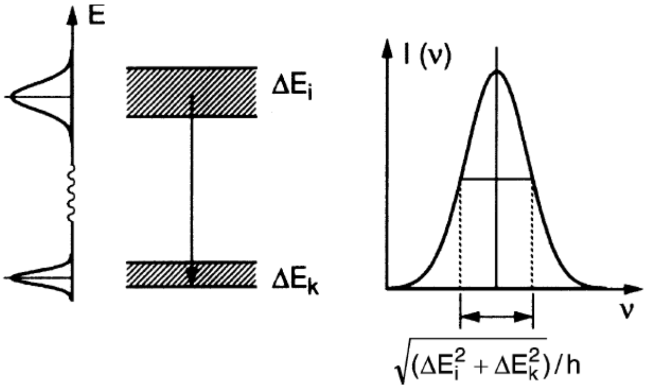
Experimental arrangement for ionization spectroscopy with pulsed laser



- experimental arrangement for photoionization spectroscopy in a molecular beam
- ionization is the most sensitive detection method
- suitable for small absorption coefficients α

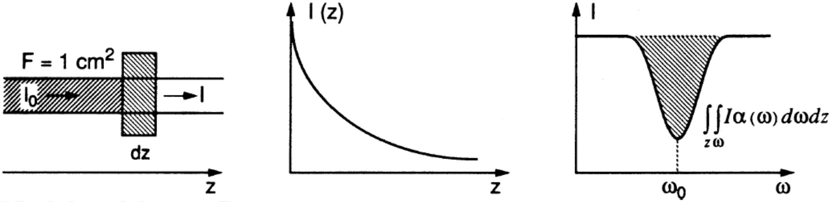
$$I = I_0 e^{-\alpha(\omega) z} \tag{51}$$

Linewidth and Lifetime



$$\omega_{ik} = \frac{E_i - E_k}{\hbar}$$
$$\delta\omega = \frac{\sqrt{\Delta E_i^2 + \Delta E_k^2}}{\hbar} \quad (52)$$

Natural linewidth of absorbing transitions



$$dI = -\alpha I dz \tag{53}$$

$$\alpha_{ik}(\omega) = \sigma_{ik}(\omega)\left[N_i - \frac{g_i}{g_k}N_k\right] \tag{54}$$

$$\alpha(\omega) = \frac{Ne^2}{4\epsilon_0 mc}\frac{\gamma}{(\omega-\omega_0)^2+(\gamma/2)^2} \tag{55}$$

Lorentzian profile with FWHM $\Delta\omega_n = \gamma$