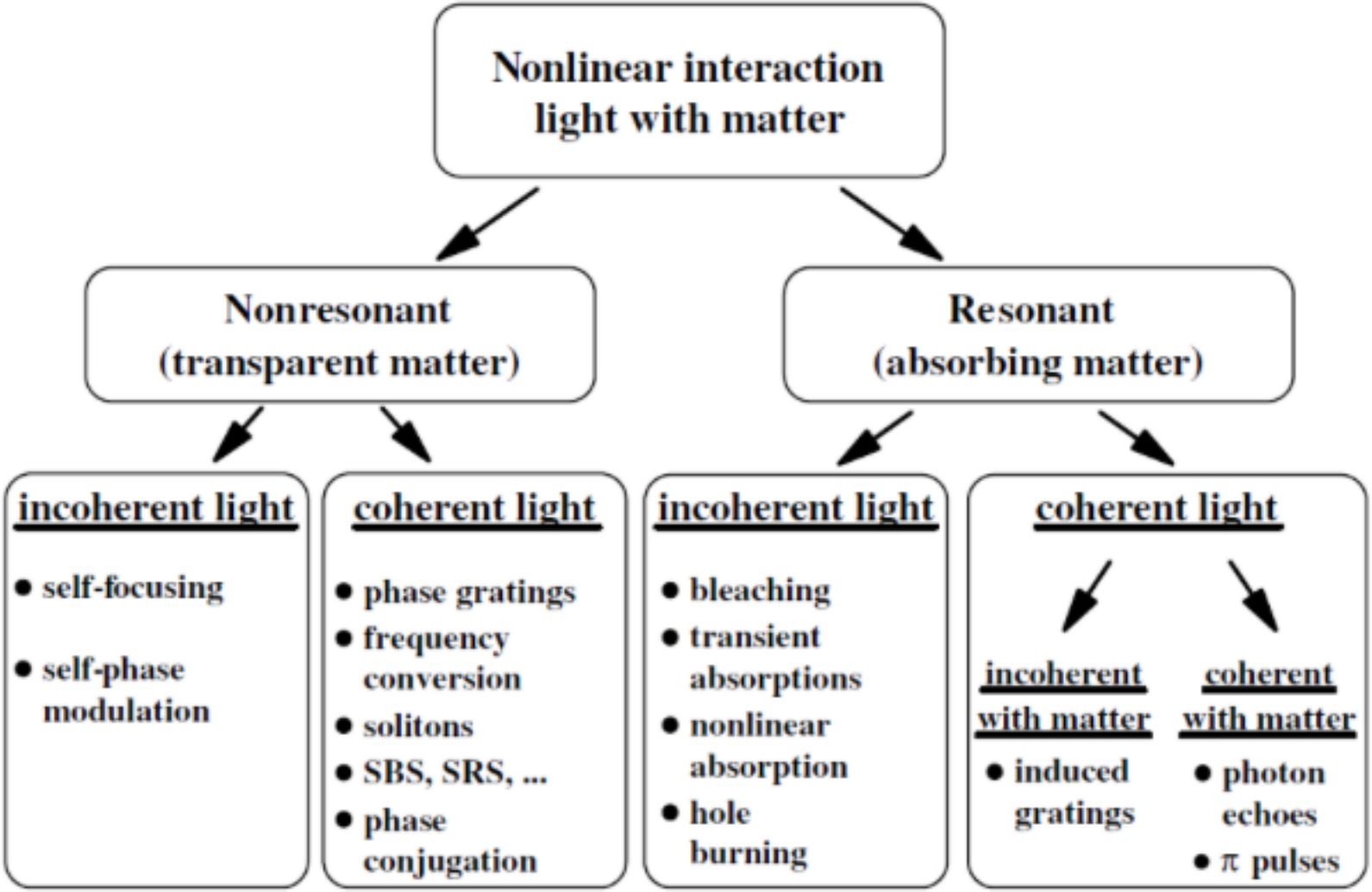
# Nonlinear Interactions of Light and Matter with Absorption

- All matter shows some absorption in almost all spectral regions as a consequence of the Lorentzian line shape of the electronic transitions with indefinite wings.
- But if the absorption coefficient is smaller than about 10−6 cm−1 the share of the resonant nonlinear interaction can often be neglected.

# General Remarks



- Nonlinear interactions in absorbing matter can show two levels of coherence:
- First, the used light fields can be coherent and thus they can produce nonlinear absorption gratings. Second, the induced dipole moment in the matter can oscillate in phase with the applied electric field.

# Homogeneous and Inhomogeneous Broadening

- In many cases matter absorption shows broad bands over a fewnm up to few 100 nm.
- For a single particle the *absorption lines may be shifted or broadened by*:
  - • particle–environment interactions;
  - • particle–particle interactions;
  - • combined transitions;
  - • Doppler shifts.

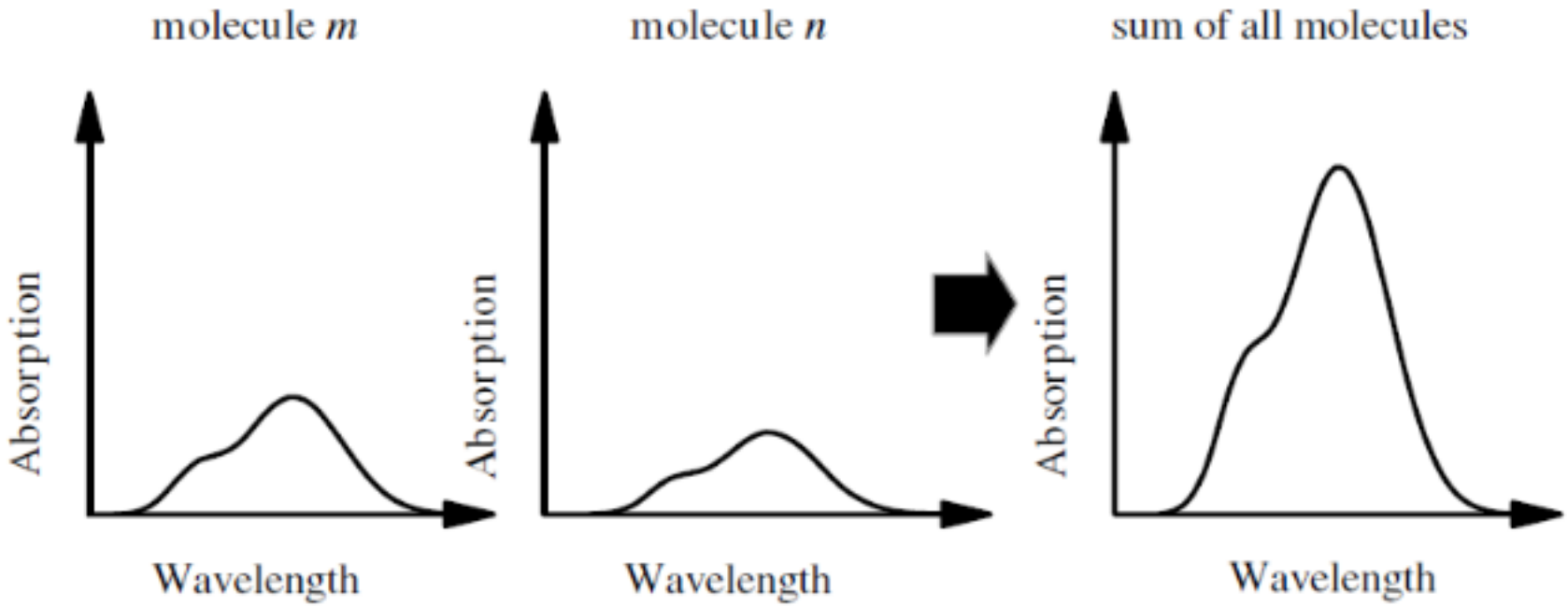
The following mechanisms may cause *additional broadening* of the observed optical absorption and emission bands of crystals or of molecular systems:

- combinations of electronic transitions;
- combinations of electronic transitions with a large number of possible simultaneous vibrational transitions;
- combinations of electronic transitions with conformational transitions of the molecules;
- participation of rotational transitions;
- molecule–solvent (intermolecular) interaction;
- molecule–molecule interactions (aggregation);
- slightly different conformations or chemical structure of the particle.

- In particular we have to be able to distinguish whether these bands are
- spectrally homogeneously or inhomogeneously broadened with respect to the
- conditions of the application or the experiment.

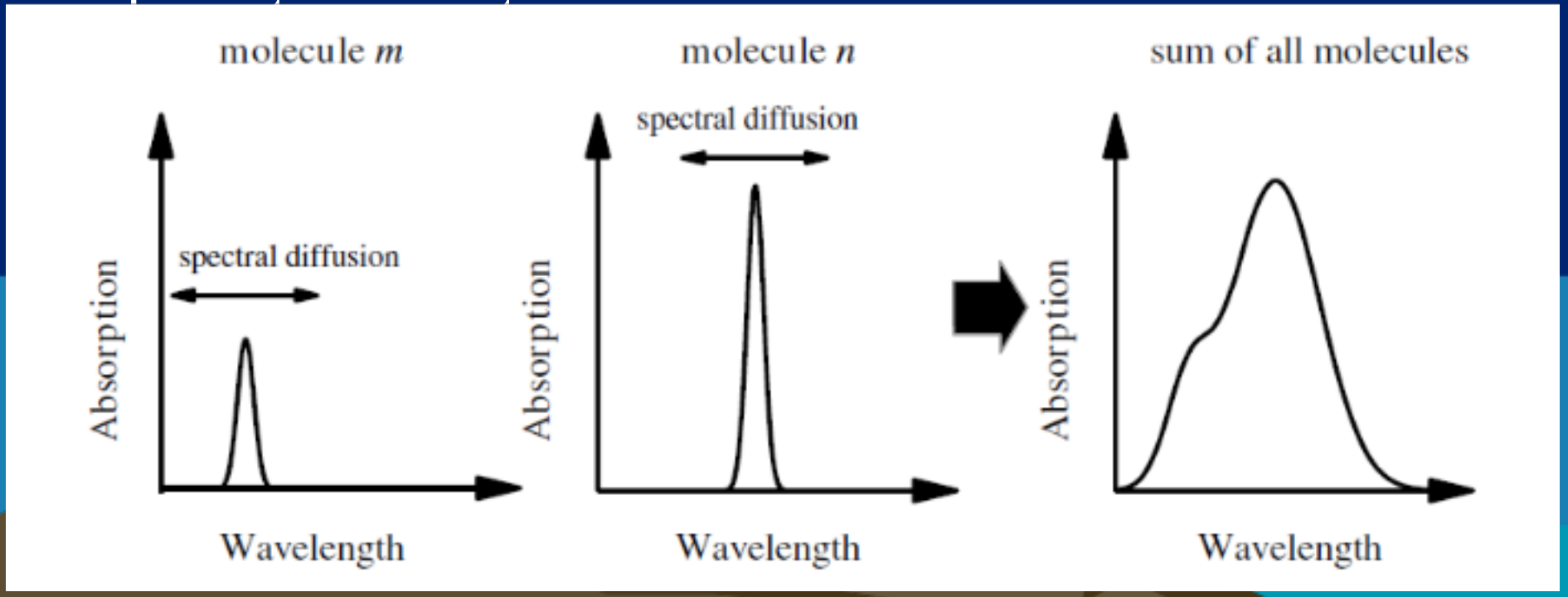
***Homogeneously broadened*** **absorption or emission bands change their amplitude but not their structure during excitation.** ***Inhomogeneously broadened*** **bands can change structure and amplitude under excitation.**

➢In the case of homogeneously broadened absorption or emission bands each particle such as, e.g. the molecules shows the same absorption spectrum and therefore the sum spectrum of the sample has the same shape as the spectra of the single particles as shown in Fig.



- Inhomogeneously broadened absorption or emission bands can be caused by slightly different particle

  states, e.g. in slightly different environments or in different vibrational states, and then the matter is called spectrally inhomogeneously broadened.
- If the particles are inhomogeneously broadened as shown in Fig. each particle shows a shifted



It is important to notice that between the different species of particles in the sample exchange processes take place. They cause spectral shifts of the absorption spectrum of the particle. The characteristic time is called

**Spectral cross relaxation time** $T3$ (*)

or sometimes in molecular systems it is called the internal vibrational relaxation (IVR) time $T$IVR if the spectral cross relaxation is assumed to be caused be coupling of the electronic transition with vibrational transitions of the molecule. Thus in time-averaged measurements inhomogeneously broadening will often not be observable.

**Inhomogeneous broadening of absorption or emission bands is a function of the time scale. It occurs for characteristic experimental times shorter than the spectral cross-relaxation time, only.**

The spectral cross-relaxation times are usually in the order of sub ps and some times longer.

Spectroscopic experiments, laser action, optical switching and nonlinear parameter determination may depend crucially on the inhomogeneous or homogeneous broadening of the material and the characteristic times of the investigation.

## Incoherent Interaction

In the case of an incoherent resonant interaction the nonlinear behavior can be described by the change of the absorption coefficient a as a function of the incident intensity of the light beam,

$$a = f\{I\} = f\{I(\boldsymbol{r}, \lambda, t, \varphi)\}$$

- The nonlinear incoherent absorption results from the change in population of absorbing or emitting energy states of the matter.
- Thus the absorption coefficient *a* for a given light beam may be written as:

$$a = \sum_m \pm\sigma_m(\lambda, \varphi, \boldsymbol{r}) N_m(I, \boldsymbol{r}, t)$$

➢ where $\sigma m$ is the cross-section of the $m$th eigenstate (or energy level) of the matter and $Nm$ is its population density.

➢ All possible absorption (+ sign) and emission (− sign) transitions have to be summed.

➢ In the most trivial approach the nonlinear absorption coefficient can be written as the first term of the series:

$$a(I) = a_0 \left\{ 1 - \frac{I}{I_{\mathrm{nl}}} \right\}$$

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**Nonlinear intensity**

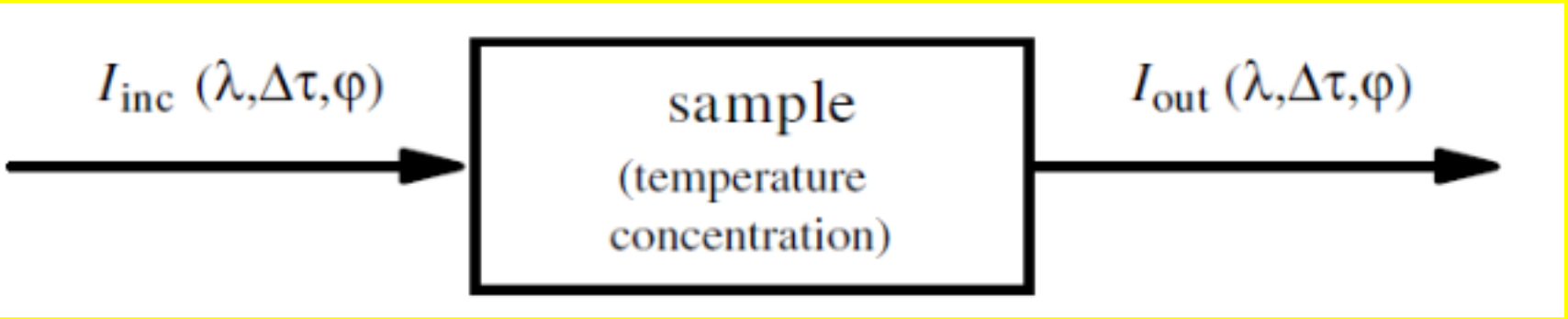
$$I_{\mathrm{nl}} = \frac{h\nu}{2\sigma\tau} \quad \text{and} \quad a_0 = \sigma N_{\mathrm{total}} \quad \text{and}$$

$$\digamma_{\mathrm{nl}} = \frac{I_{\mathrm{nl}}}{h\nu} = \frac{1}{2\sigma\tau}$$

- where $\sigma$ is the cross-section of the active transition, $\tau$ the recovery time of the absorption of this transition, $\nu$ its frequency and $N$total the population densityof the absorbing state without excitation. The intensity $\digamma_{\mathrm{nl}}$ measured as the photon flux density in photons cm−2 s−1.
- The following effects can be obtained:
  - bleaching;
  - general nonlinear transmission including darkening;
  - transient absorptions – excited state absorptions (ESA);
  - stimulated emission – superradiance – laser action;
  - spectral hole burning.

# Bleaching

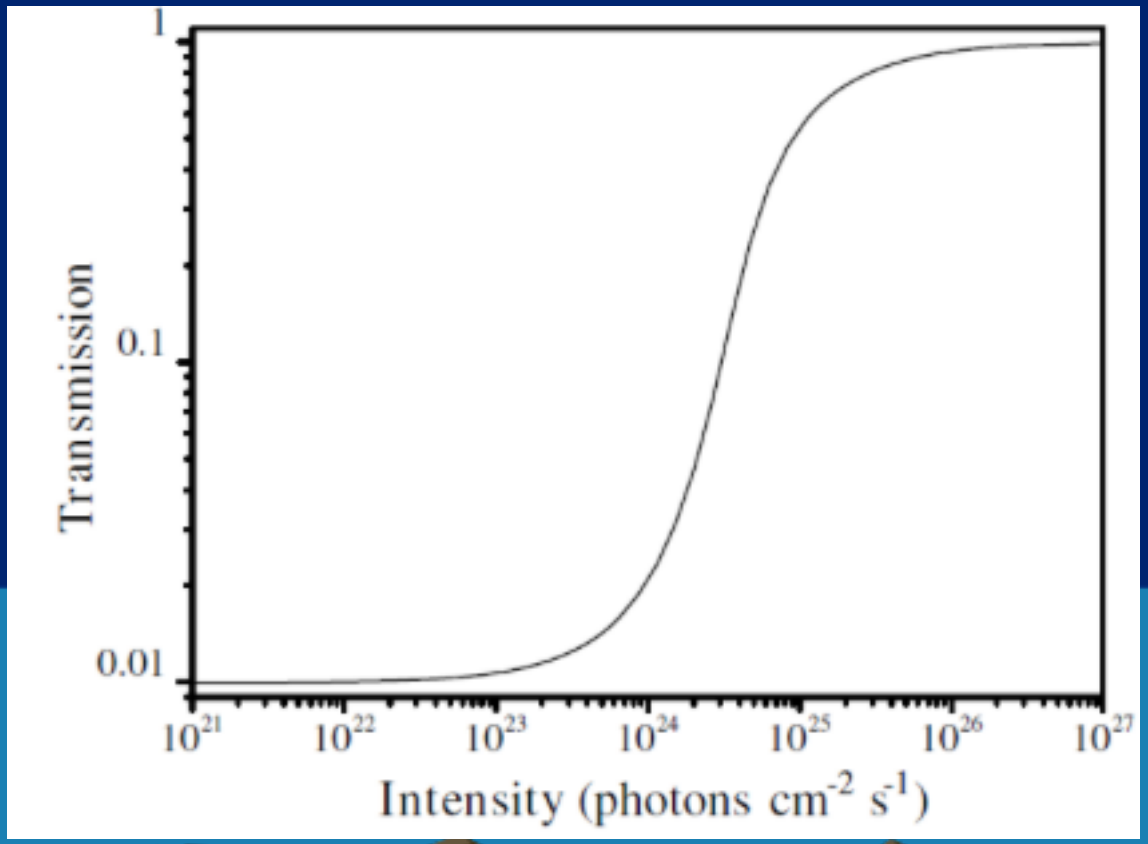
- Optical bleaching of matter is observable in simple one-beam experiments measuring the transmission of the sample as a function of the incident intensity




**Transmission** $$T = \frac{I_{out}(t_m)}{I_{inc}(t_m)}$$

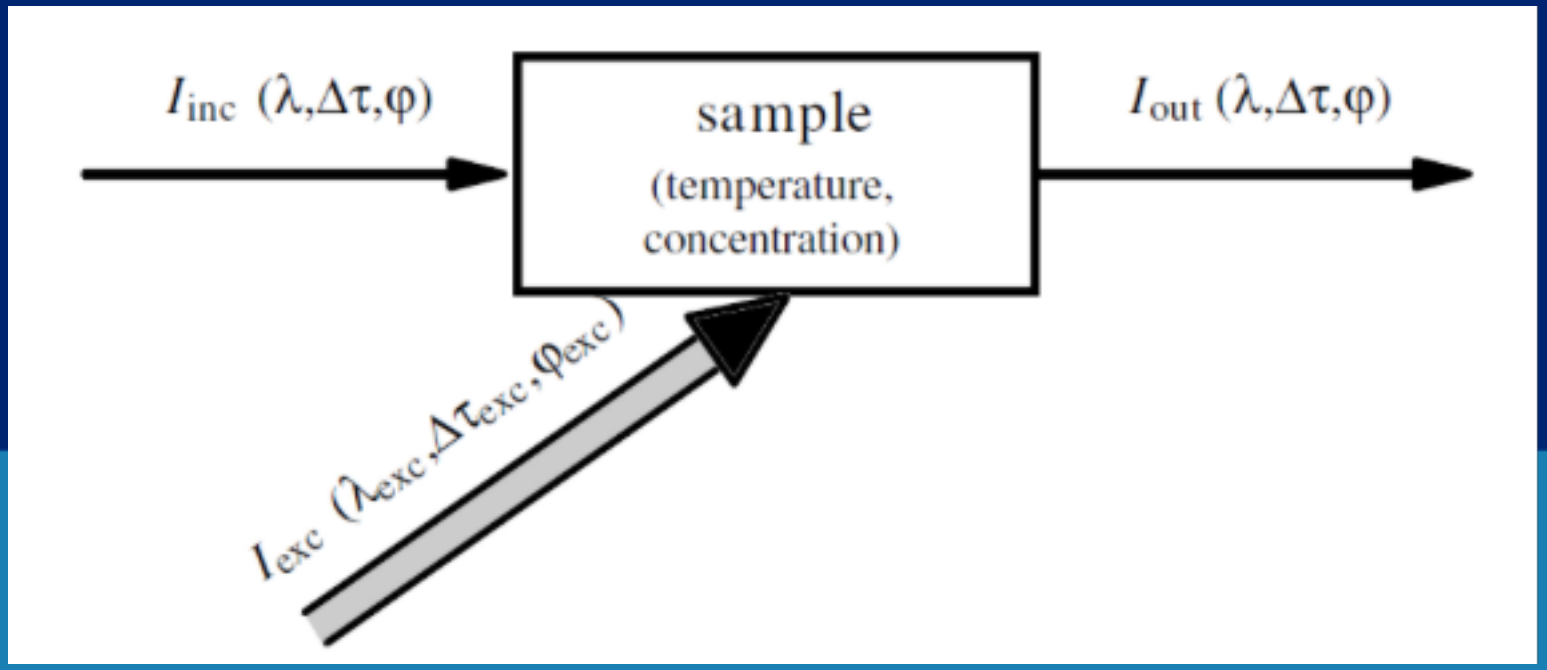
In experiments with ps or fs pulses the temporal pulse shape cannot be measured electronically.

At low intensities the transmission is constant, as expected, and then the transmission increases in this two-level model up to 1. The parameters are used as given in the figure caption for the two-level scheme.



# Transient Absorption: Excited State Absorption (ESA)

- A large variety of nonlinear absorption effects can be obtained in pump–probe experiments with at least two beams

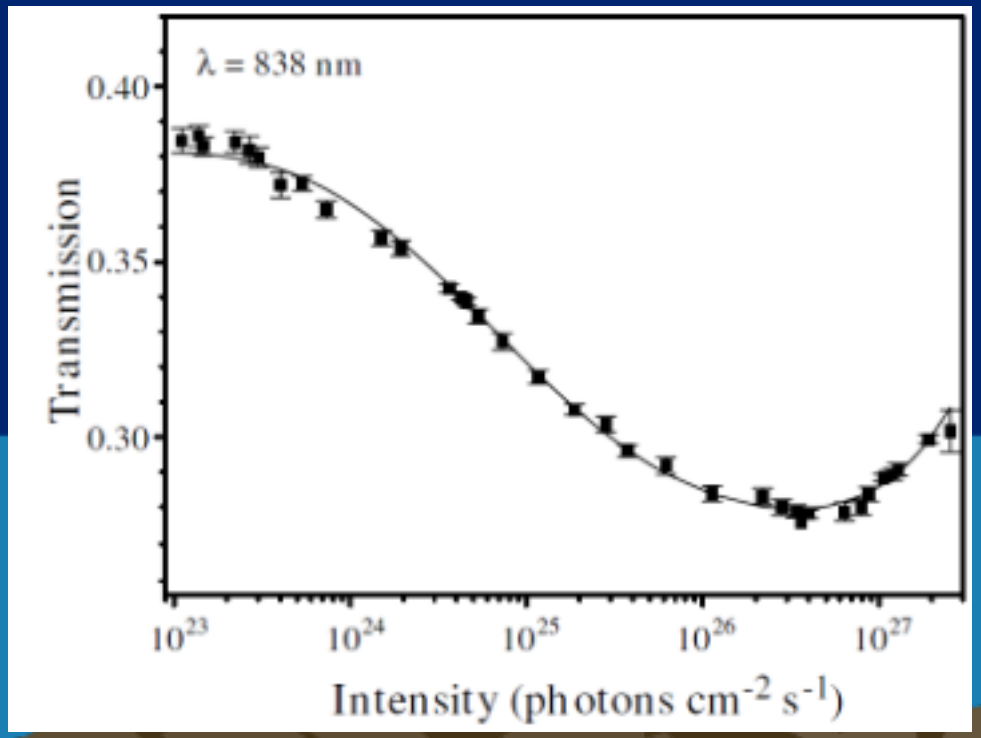


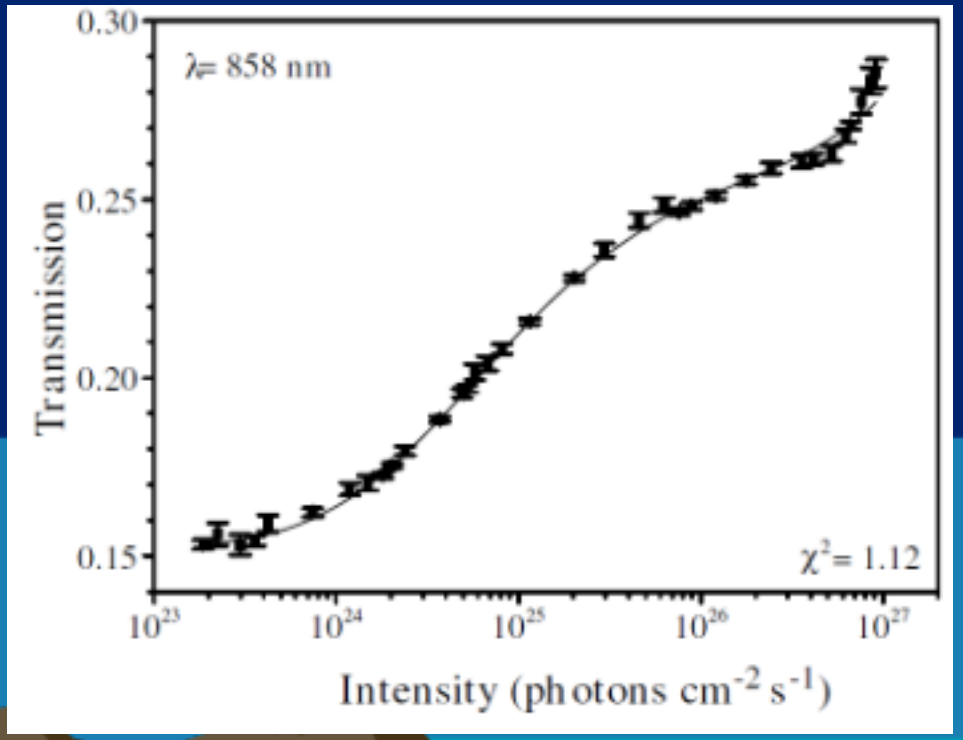
- The nonlinear effect is produced by a strong pump beam which populates excited states in the sample.
- This alteration of the sample has a large variety of new properties generated by the exciting light.
- The choice of the pump light parameters allows the appropriate population of all kinds of special material states with different new absorption characteristics, with life times from a few fs to hours, and so on.
- The exciting light can be built from two or more different light beams for multiple excitation of the sample.
- But in any case the probe light intensity has to be small enough not to disturb the sample itself.

## Nonlinear Transmission

- The nonlinear transmission of absorption bands especially of organic materials can be much more complicated than the described bleaching.
- In many cases an excited state absorption (ESA) occurs in the same wavelength range as the ground state absorption (GSA) with sometimes an even stronger cross-section than the GSA.
- The combination of bleaching and new transient absorptions can lead to quite complicated functions of the transmission as a function of the incident intensity in the nonlinear range.
- Besides variations in the slope of the bleaching curve the new nonlinear activated absorption can even cause darkening of the sample

- But the same sample shows different behavior with a 20nm longer excitation wavelength.
- Therefore all kinds of transmission graphs as functions of the intensity with maxima, minima and plateau are possible.
- The evaluation of the nonlinear transmission curve allows the identification of excited state absorption.

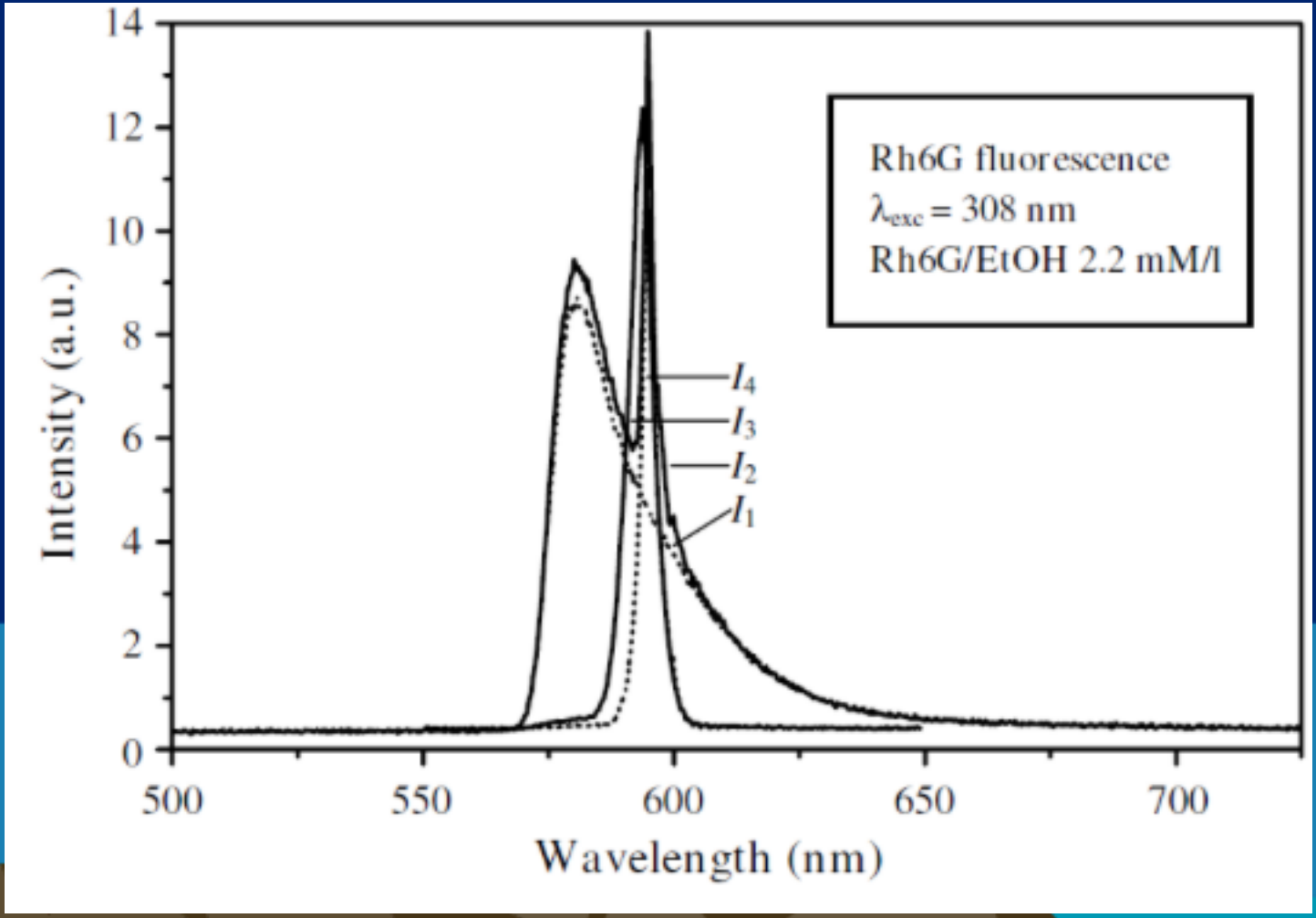


# Stimulated Emission: Superradiance: Laser Action

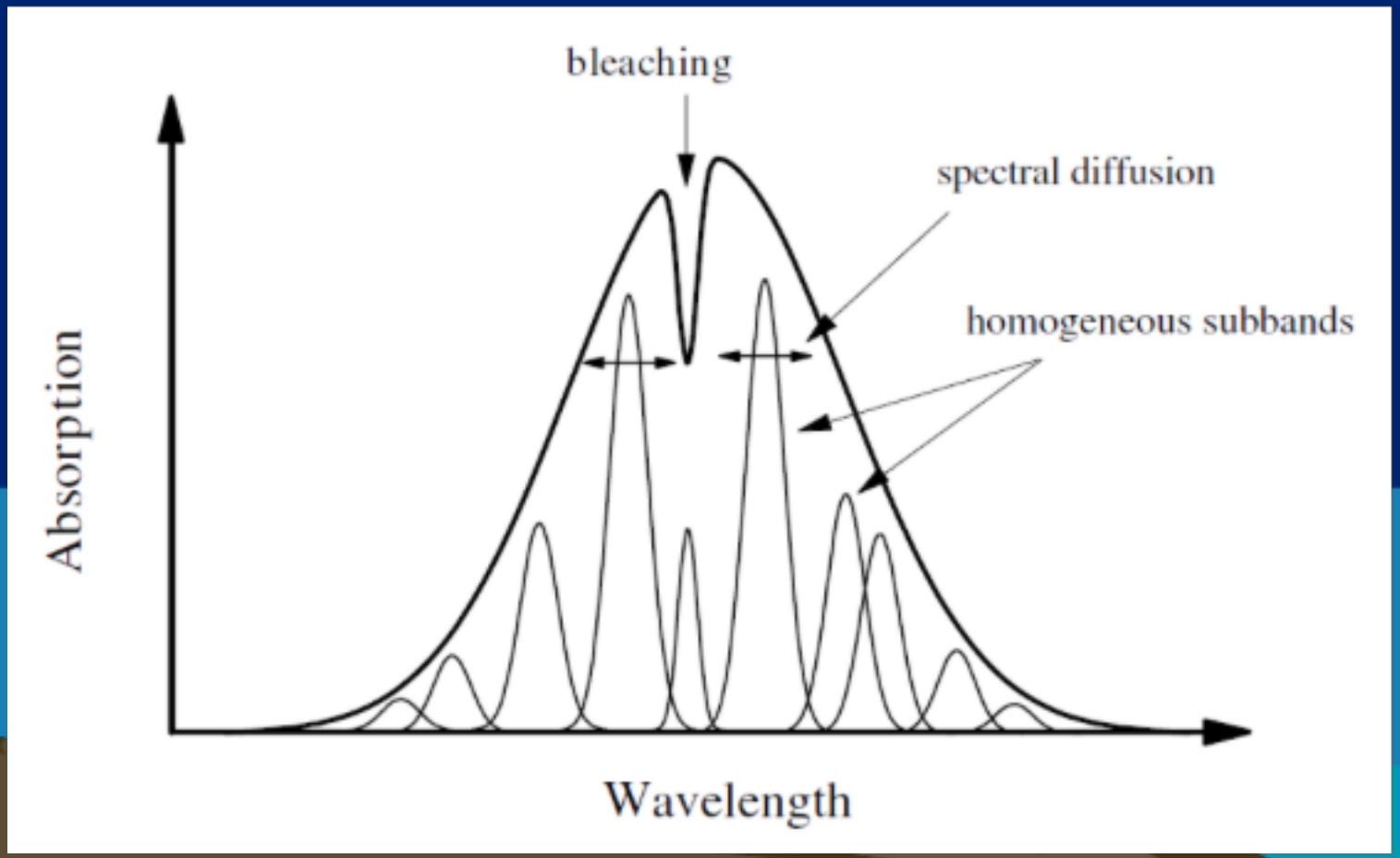
- In other photonic applications or in nonlinear spectroscopy stimulated emission will not always be in the focus of the experiment.
- Unexpected stimulated emission such as superradiance or laser action will change the properties of the nonlinear interaction drastically.
- Wide fluorescence bands will narrow to the laser line, the lifetime of the excited state can be reduced by many orders of magnitude and polarization conditions will be changed.

- The observation of stimulated emission is not always easy. The transition from fluorescence to superradiance happens in practice almost continuously



# Spectral Hole Burning

If the optical transition of the matter is inhomogeneously broadened the change of the transmission will be different for the wavelength of the exciting beam and in the spectral neighborhood



The relation of bleaching at the excitation wavelength and in the spectral surroundings of it will depend on the relation of the spectral diffusion or spectral cross-relaxation time T3 on one hand and the energy relaxation time T1 on the other.

If the spectral cross-relaxation is much slower than the energy relaxation $T3 >> T1$ maximum hole burning will be observed and thus the bleaching at the excitation wavelength will be a maximum and the rest of the absorption band will be unchanged.

If the spectral cross-relaxation is much faster than the energy relaxation $T3 << T1$ almost no hole burning can be obtained, even using high intensities in the nonlinear experiments.

The homogeneous linewidth determines the minimum hole width.

The mechanisms of spectral hole burning are at least as diverse as the reasons for inhomogeneous broadening.

Finally, chemical and photo-physical hole burning can be distinguished with drastically different hole life times.

Spectral hole burning may find photonic applications in communications such as in spectrally coded switching and storage.

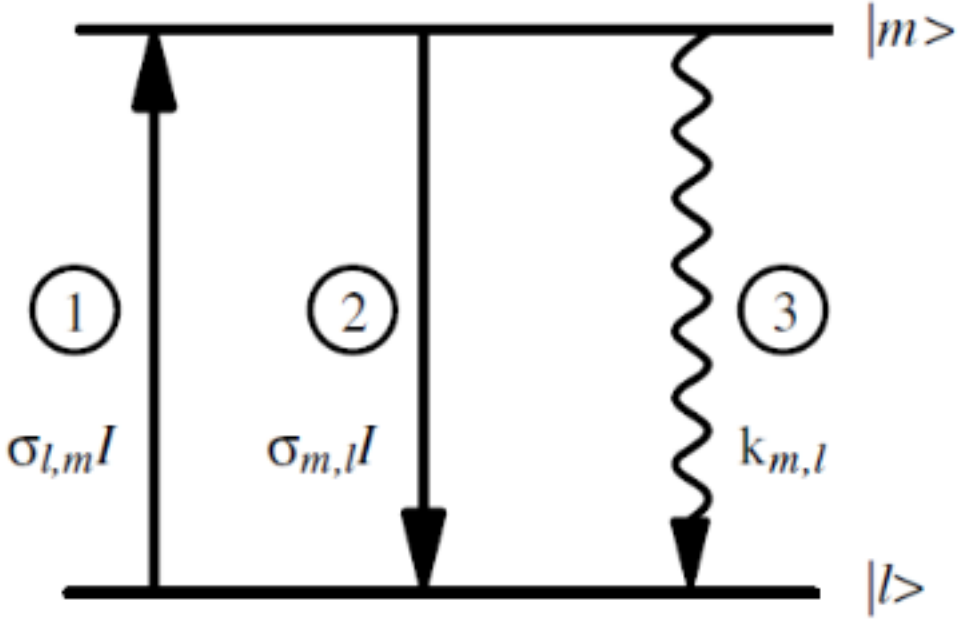
# Description with Rate Equations

The nonlinear interaction of a light beam with matter can be well described with rate equations if coherence effects are not important.

This is usually fulfilled if the phase relaxation time T2 is much shorter than the incident pulse duration, the inverse pump rate $1/(\sigma \bar{I})$ and the decay times $\tau$ .

## Basic Equations

Between the two energy states or energy levels l and m of matter



In an easily understandable way each single transition of one particle will decrease the population density of the initial state by 1 and also increase the final state by 1:

(1) *absorption* from $l$ to $m$ ($N_l \rightarrow N_m$):

$$\frac{\partial N_l}{\partial t} = -\sigma_{l,m} \text{Ł} N_l \quad \text{and} \quad \frac{\partial N_m}{\partial t} = +\sigma_{l,m} \text{Ł} N_l$$

(2) *stimulated emission* from $m$ to $l$ ($N_l \rightarrow N_m$):

$$\frac{\partial N_l}{\partial t} = +\sigma_{m,l} \text{Ł} N_m \quad \text{and} \quad \frac{\partial N_m}{\partial t} = -\sigma_{m,l} \text{Ł} N_m$$

(3) *spontaneous relaxation* from $m$ to $l$ ($N_l \rightarrow N_m$):

$$\frac{\partial N_l}{\partial t} = +k_{m,l} N_m \quad \text{and} \quad \frac{\partial N_m}{\partial t} = -k_{m,l} N_m$$

with cross-sections $\sigma_{l,m}$ and $\sigma_{m,l}$, the intensity (photon flux density) I and decay rates $k_{m,l}$ which are the inverse of the decay times $\tau_{m,l}$:

$$k_{m,l} = \frac{1}{\tau_{m,l}}.$$

- The decay rates of different channels between the same states, e.g. spontaneous emission and radiationless decay, can simply be added to the total decay rate:

$$k_{m,l}^{\text{total}} = k_{m,l}^{\text{spont.emission}} + k_{m,l}^{\text{radiationless}} + \dots$$

# Coherent Light Fields

If two or more coherent intensive light beams are applied in incoherent interactions in the absorption range of the matter the nonlinear effects will be spatially structured by the interference pattern of the light. the intensity pattern has to be determined in its nonlinear interaction with the matter absorption.

This can demand extensive numerical calculations of the coupled partial differential equations for the time-dependent intensity field in three dimensions

$$I(\boldsymbol{r},t) = \frac{c_0 \varepsilon_0 n}{2h\overline{\nu}} \left\{ \sum_i \boldsymbol{E}_i(\nu_i, \boldsymbol{k}_i, \varphi_i) \right\}^2$$

coupling with the absorptive transitions of the matter:

$$\left( \frac{\partial}{\partial z} + \frac{1}{c} \frac{\partial}{\partial t} \right) I(\boldsymbol{r},t) = I(\boldsymbol{r},t) \sum_l \sum_{m(>l)} \left( -\sigma_{l,m} N_l(\boldsymbol{r},t) + \sigma_{m,l} N_m(\boldsymbol{r},t) \right)$$

(5

But the dependency in space can be more complicated:

$$\frac{\partial}{\partial t}N_l(\boldsymbol{r},t) = \boldsymbol{\mathit{f}}(\boldsymbol{r},t)\sum_{m(\neq l)}\{-\sigma_{l,m}N_l(\boldsymbol{r},t)+\sigma_{m,l}N_m(\boldsymbol{r},t)\}$$

$$= +\sum_{m(\neq l)}\{-k_{l,m}N_l(\boldsymbol{r},t)+k_{m,l}N_m(\boldsymbol{r},t)\}$$

$$\sum_{l=1}^{n}N_1(\boldsymbol{r},t) = N_{\mathbf{total}}(\boldsymbol{r},t)$$

This incoherent nonlinear interaction of coherent light beams with absorbing matter has found several applications in photonics, especially using light patterns with a well-defined spatial grating structure.

Bleaching or nonlinear transmission of matter will lead to spatial transmission gratings of the sample.

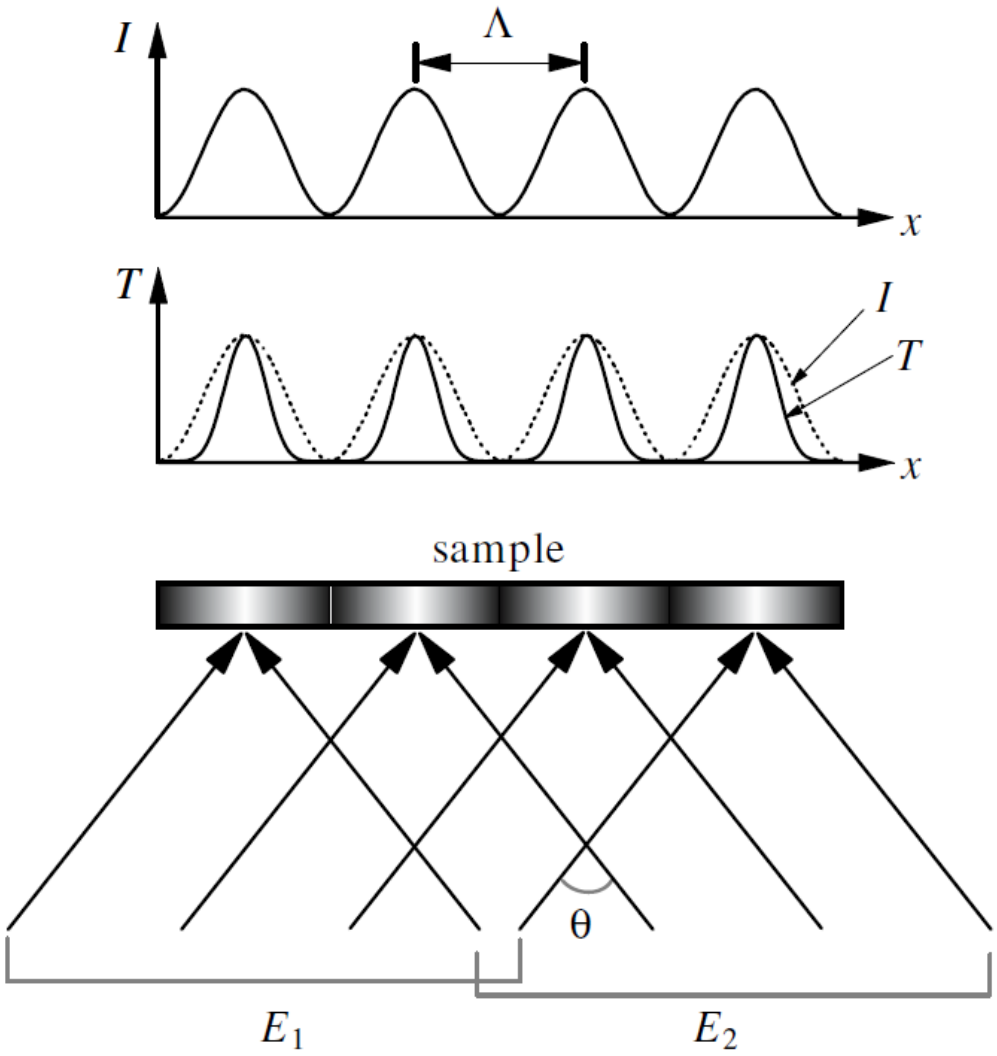
These can be used for deflection of light beams in optical switching.

If the modulation results from the standing wave in a laser resonator spatial hole burning can occur and can cause instabilities in laser operation.

# Induced Transmission and Excited State Absorption Gratings

In the simplest case two equal spectrally degenerate light waves with parallel polarization but different propagation direction are used for illumination of the sample.

In the interference region of these two intensive pump beams a spatial sine grating modulation for the intensity pattern would occur without the interaction




**At positions of high excitation intensities the matter absorption at the excitation wavelength can be bleached and/or new excited state absorptions may occur at other wavelengths.**

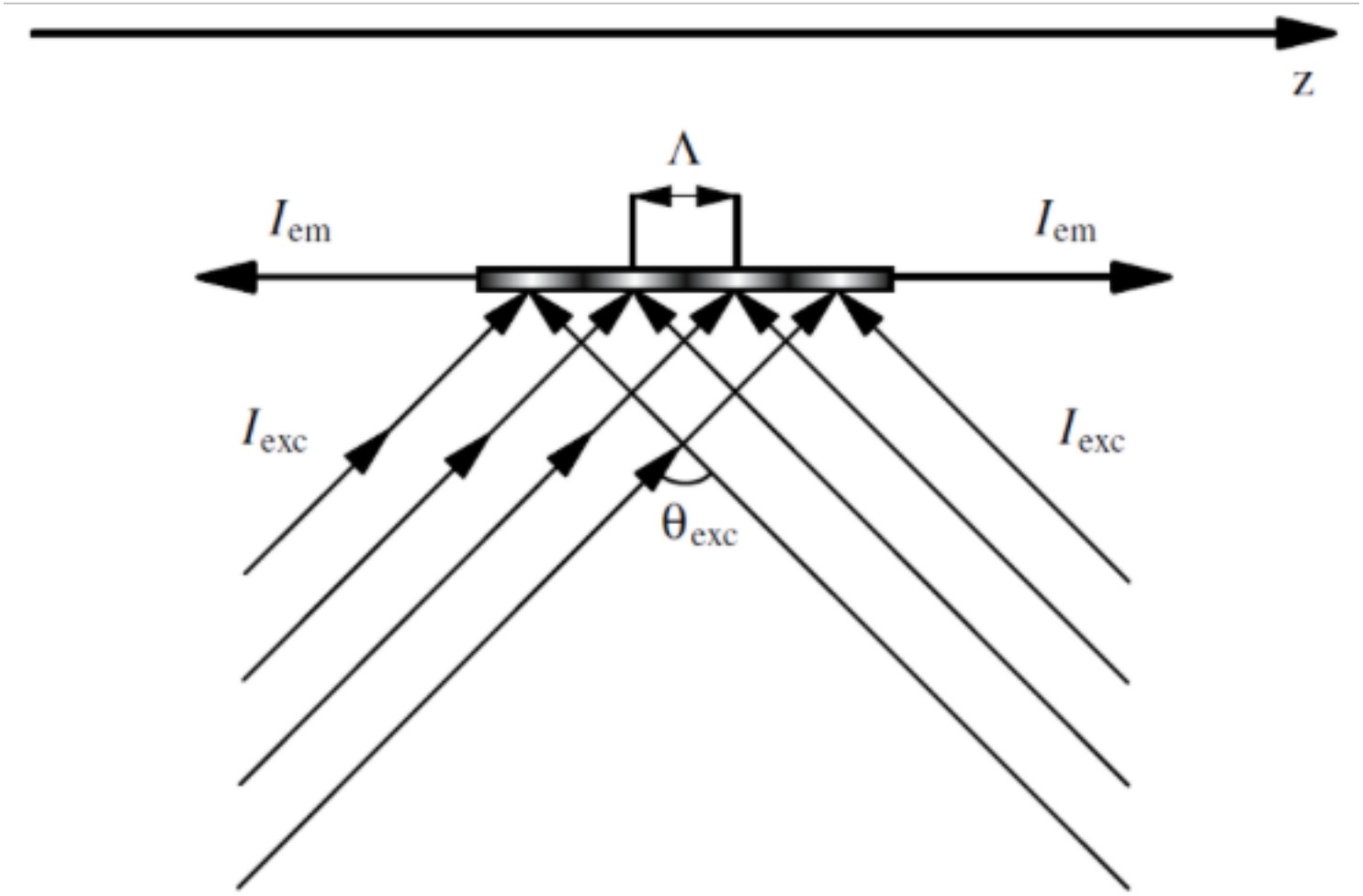
The distance Λ of the grating structure follows from the angle θ between the beams and the wavelength λexc of the pump light as:

$$\Lambda = \frac{\lambda_{\text{inc}}}{2 \sin\left(\frac{\theta}{2}\right)}.$$

# Induced Inversion Gratings

- If laser active material is excited by the interference pattern of the pump beams an inversion grating may be generated.

**The laser action will be determined from this structure and especially the longitudinal modes may be selected.**



Because of the interference of the laser light along the z axis in the sample only a certain wavelength λDFBL can be amplified. The gain period is determined by the angle θexc between the two pump beams and their wavelength λexc:

$$\lambda_{\mathrm{DFBL}} = \frac{n_{\mathrm{mat}} \lambda_{\mathrm{exc}}}{2 \sin\left(\frac{\theta_{\mathrm{exc}}}{2}\right)}$$

with refractive index of the material $n_{mat}$.

- The spectral width of the laser is approximately given by:

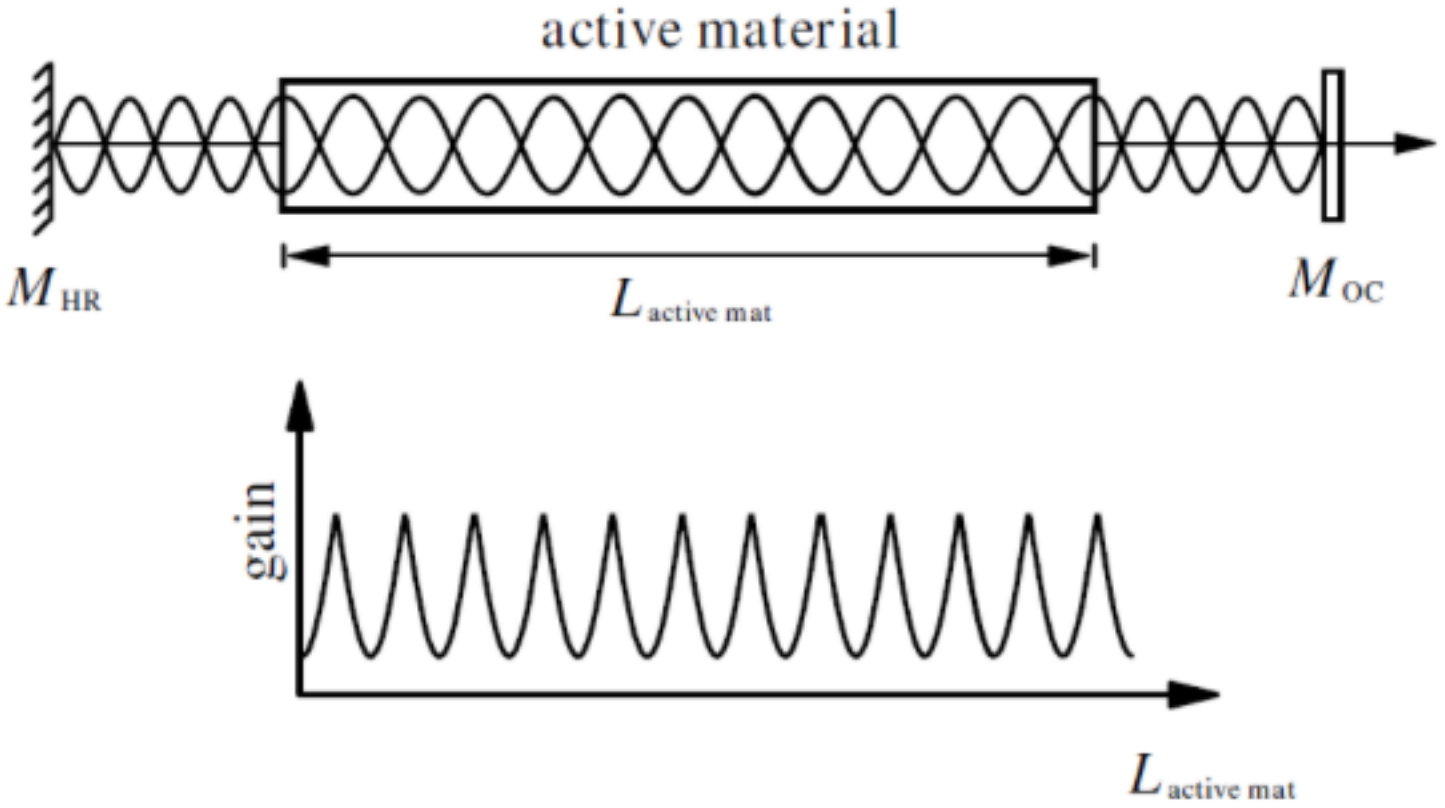
$$\Delta\lambda_{\mathrm{laser}} = \frac{\lambda_{\mathrm{laser}}^2}{2L_{\mathrm{exc}}}$$

where Lexc is the length of the excited matter which determines the number of “grating lines”.

# Spatial Hole Burning

If the inversion is depopulated by the standing wave of the laser radiation in the resonator the effect is called spatial hole burning.

In this case the positions of the intensity maxima are coupled with the minima of the inversion and thus the minima of the gain g.



The standing wave occurs in the laser resonator as a result of the steadystate field condition with nodes of the electric field at the mirror surfaces.

Thus the optical length Lres of the resonator defines the possible wavelengths λlaser(p) of the axial or longitudinal laser modes:

$$\text{possible axial modes} \quad \lambda_{\text{laser}}(p) = \frac{2L_{\text{res}}}{p}$$

- where the optical length results:

$$L_{\text{res}} = L_{\text{geom}} + L_{\text{active mat}}(n_{\text{active mat}} - 1)$$

- Because the gain minima are differently located for the different axial modes other possible axial modes within the gain profile will start to oscillate.
- In consequence an oscillation between the axial modes can take place (mode hopping) and the laser output power will fluctuate.

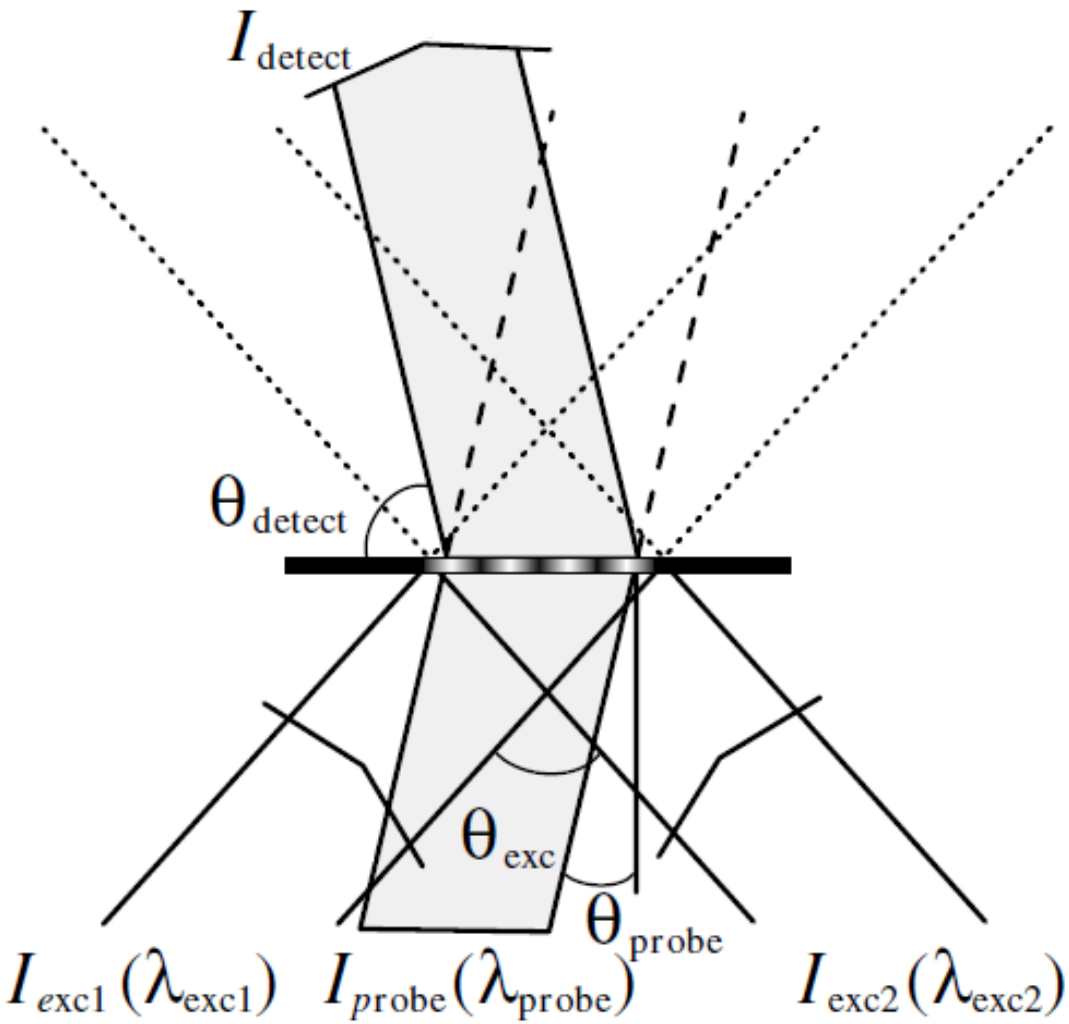
If the gain profile of the active matter is spectrally inhomogeneously broadened the different axial modes may oscillate completely independently and laser intensity fluctuations can take place for each axial mode separately only within the homogeneous linewidth.

Spatial hole burning in laser resonators can be avoided by preventing the standing waves in the laser.

Several types of resonators are known to solve this problem. Examples are ring resonators with an optical valve forcing the light wave to travel in one direction only,

# Induced Grating Spectroscopy

- The nonlinear optical properties of matter especially of organic molecules can be investigated by inducing a transmission grating, an excited state absorption grating or an inversion grating in the sample with two pump pulses and using a third probe light beam for spectroscopy .
- The probe light will be diffracted at the induced grating structure if the intensity of the two pump beams is high enough to reach the nonlinear range.
- The experiment can be set up in a way that no pump light will be detectable in the observation direction of the scattered probe light and without nonlinear interaction also no probe light will be scattered.
- For this purpose the angles of the incident pump beams and probe light beam have to be chosen appropriately.




Because of this high sensitivity this type of spectroscopy (see Sect. 7.8.3,

p. 609) via induced nonlinear optical gratings can be used for the observation

of very weak transient absorption changes in the range below 10−4 even in

ultra-short pulse measurements with ps or fs time resolution.

# Coherent Resonant Interaction

If dephasing in the matter after excitation is slower than the characteristic time constant of the interaction, such as, e.g. the pulse duration of the coherent laser light, coherent interaction can take place and new effects are observable

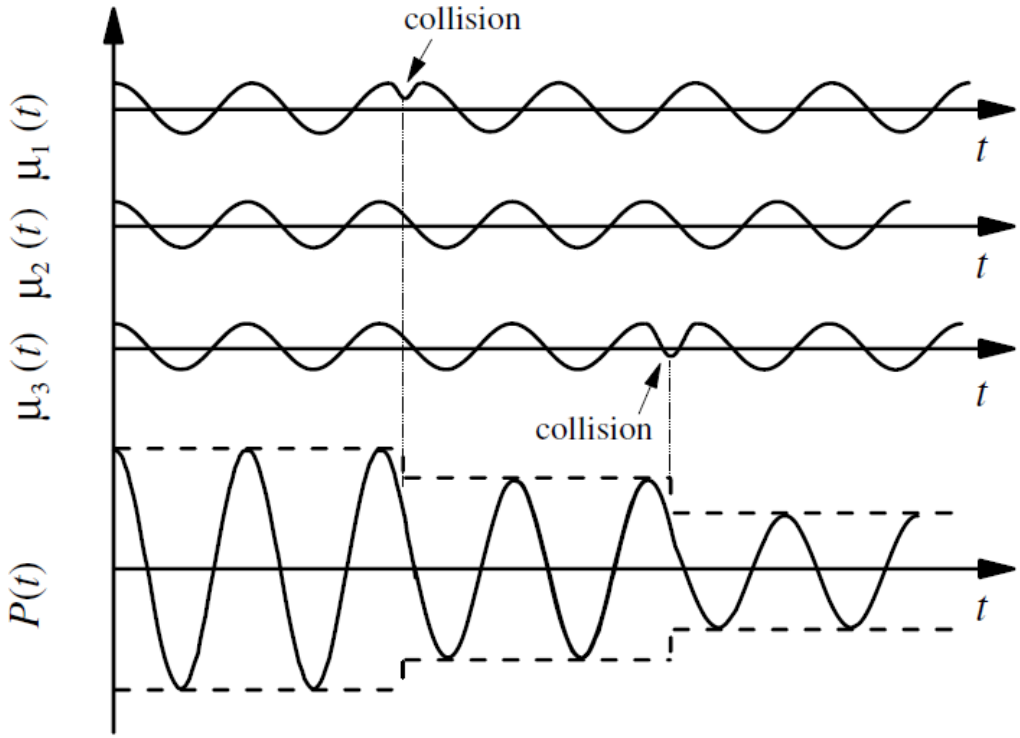
## Dephasing Time T2

The coherent electric field of the excitation light beam induces electrical transition dipole moments μm in each particle.

The macroscopic nonlinear polarization Pnl is the sum over all these microscopic dipole moments.

In the case of coherent interactions these dipole moments oscillate with fixed phases in relation to each other and in phase with the electric field of the light wave.

This takes place as long as the system is not distorted.




The dephasing time T2 is defined as the time during which the macroscopic polarization is decreased by 1/e after coherent excitation at time t = 0:

$$\textbf{dephasing time } \boldsymbol{T_2} \quad P_{\mathrm{nl}}(t) = P_{\mathrm{nl}}(0)\,\mathrm{e}^{-t/T_2}.$$

These dephasing times are usually smaller than 10−12 s for molecules at room temperature and usually in other materials shorter than μs. Only at times shorter than this dephasing time coherent interaction can take

place.

# Damped Rabi Oscillation and Optical Nutation

If a near-resonant light beam with electric field amplitude Eexc and frequency νexc is applied the transmission of the sample will be modulated with the Rabi frequency ΩR:

$$\textbf{Rabi frequency} \quad \Omega_{\mathrm{R}} = \sqrt{2\pi(\nu_{\mathrm{exc}} - \nu_0)^2 + \left(\frac{\mu_{ba} E_{\mathrm{exc}}}{2\pi h}\right)^2}.$$

- The damping time τR is given for the exponential decay after resonant excitation in this case:

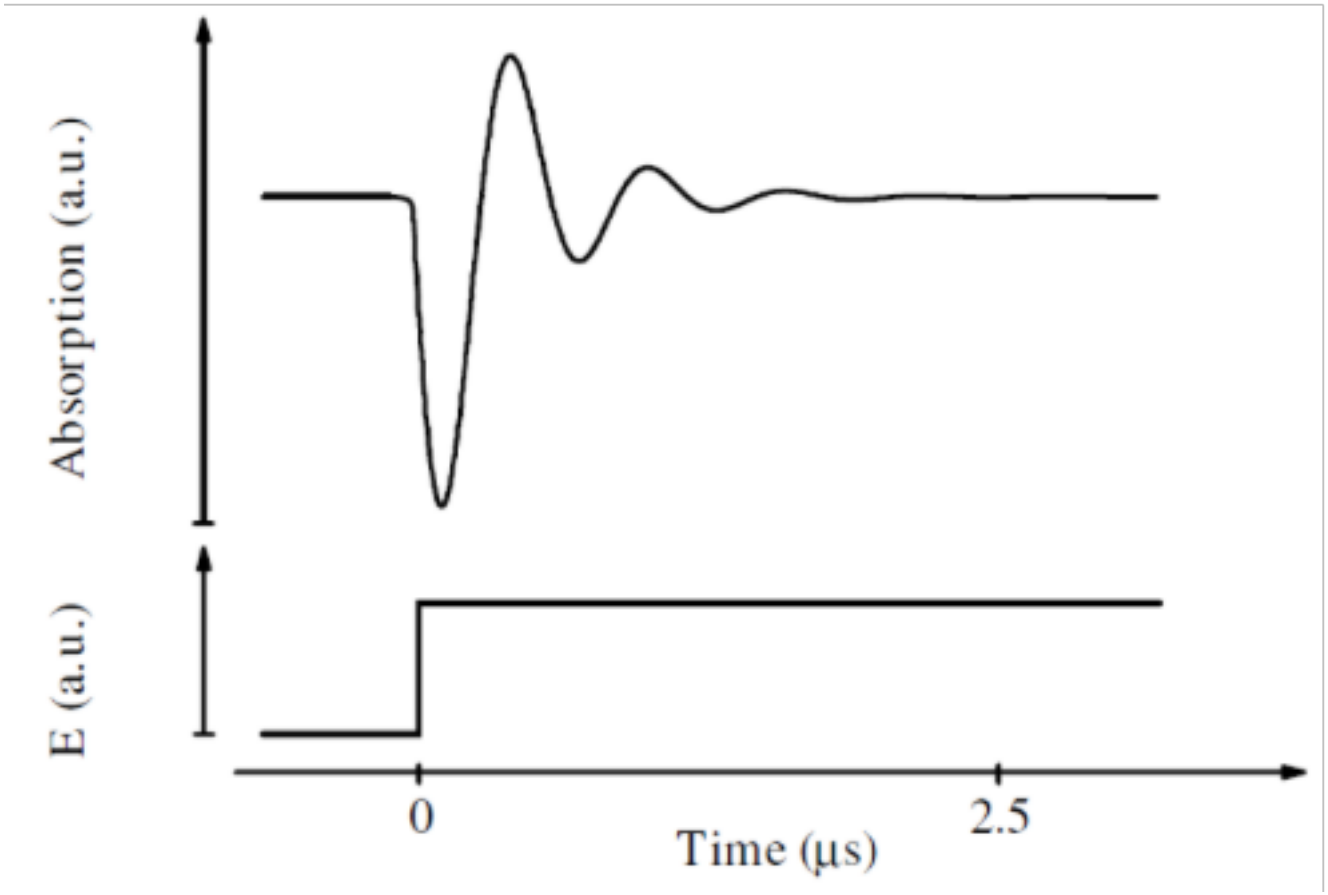
$$\text{damping time} \quad \tau_{\mathrm{R}} = 2\left(\frac{1}{2T_1} + \frac{1}{T_2}\right)^{-1}$$

and nonresonant excitation results in a slightly nonexponential decay of the form:

$$\mu_{ba} \propto \frac{\mathrm{e}^{-t/\tau_{\mathrm{R}}}}{\left[1 + C_{\mathrm{R}} t^2 (\nu_{\mathrm{exc}} - \nu_0)^4\right]^{1/4}}$$

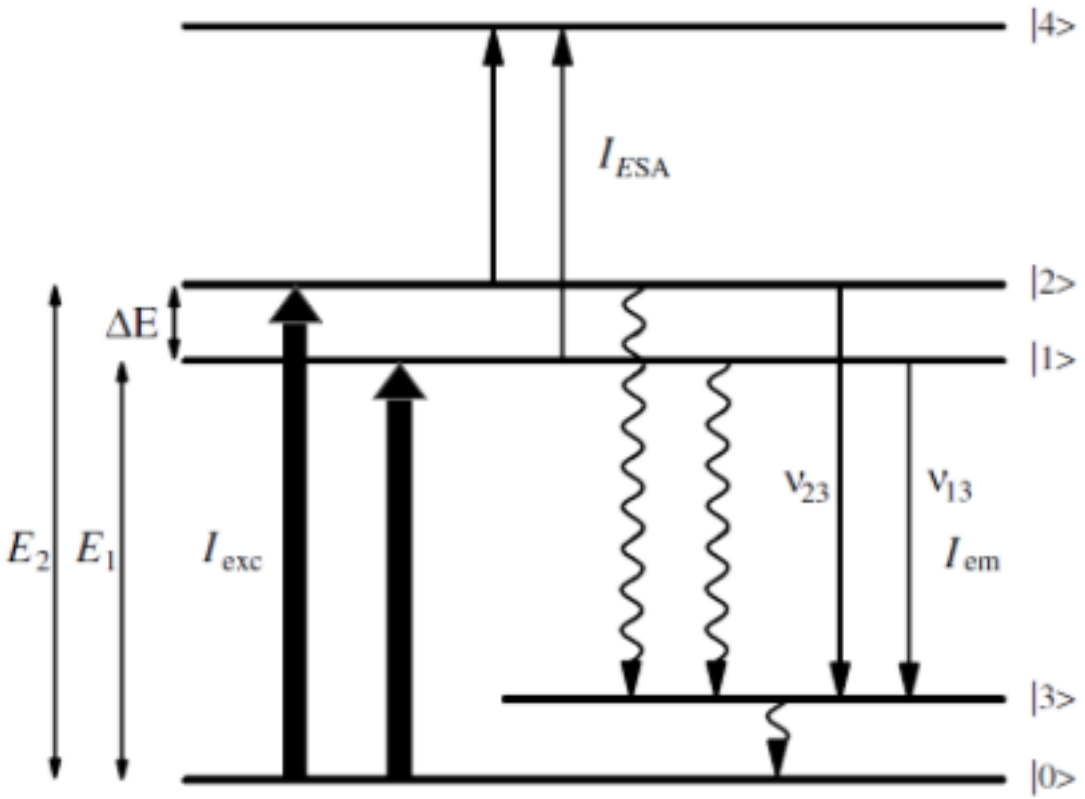
To obtain the Rabi oscillations in the transmission the damping time has to be longer than the inverse Rabi oscillation frequency.

The observable effect of the periodic absorption (particles in the ground state) and amplification (particles in the excited state) of the incident light as a function of time is observable as optical nutation.



# Quantum Beat Spectroscopy

If the particles have two closely spaced energy levels such as, e.g. two excited states and the exciting light excites both levels at the same time with a spectrally broad short laser pulse a coherent interaction between these two states will occur.

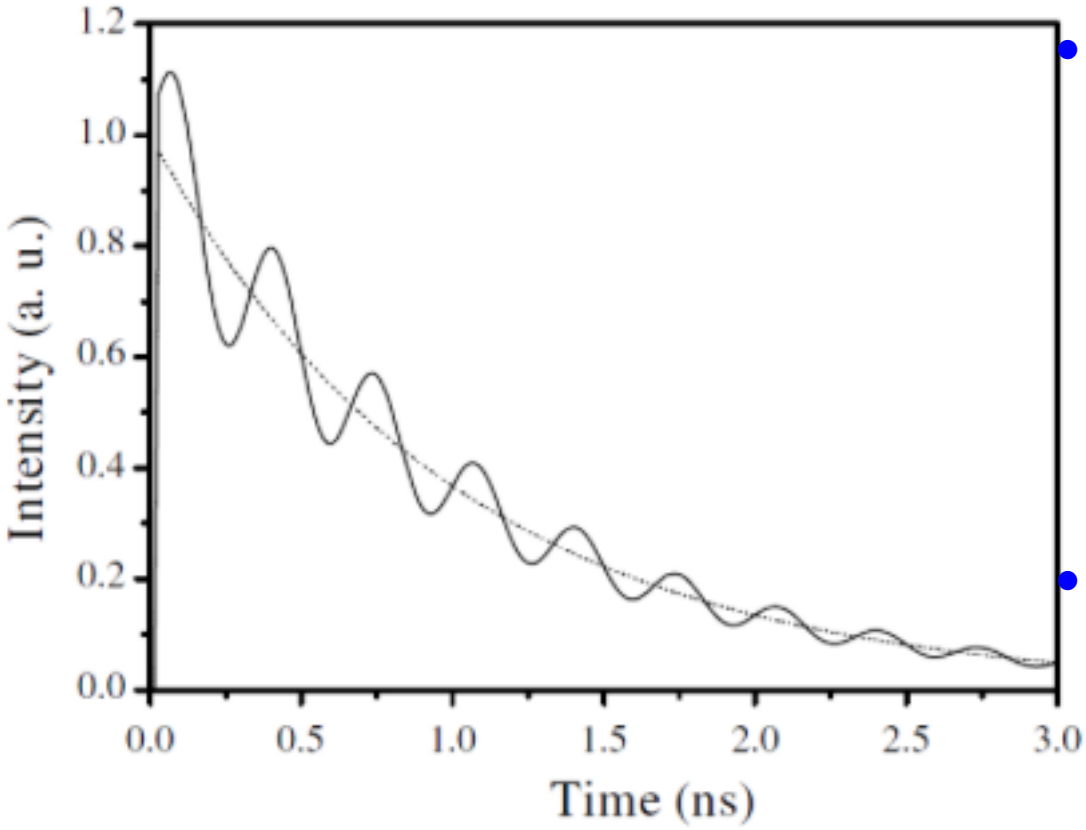



**As a result the absorption and emission of this particle will show temporal oscillations which are known as quantum beats.**

An oscillation with the beat frequency Δν:

$$I_{\mathrm{em}}(t), I_{\mathrm{ESA}}(t) \propto \mathrm{e}^{-t/\tau_{\mathrm{exc}}}[C_1 + C_2 \cos(2\pi\Delta\nu t)].$$

This modulation in the decay function for the population of this doublet of states represents the coherent superposition of the two quantum states.




Therefore from this temporal measurement the energy difference of the two states can be determined with higher accuracy the closer the levels are.

This method allows a resolution better than Doppler broadening.

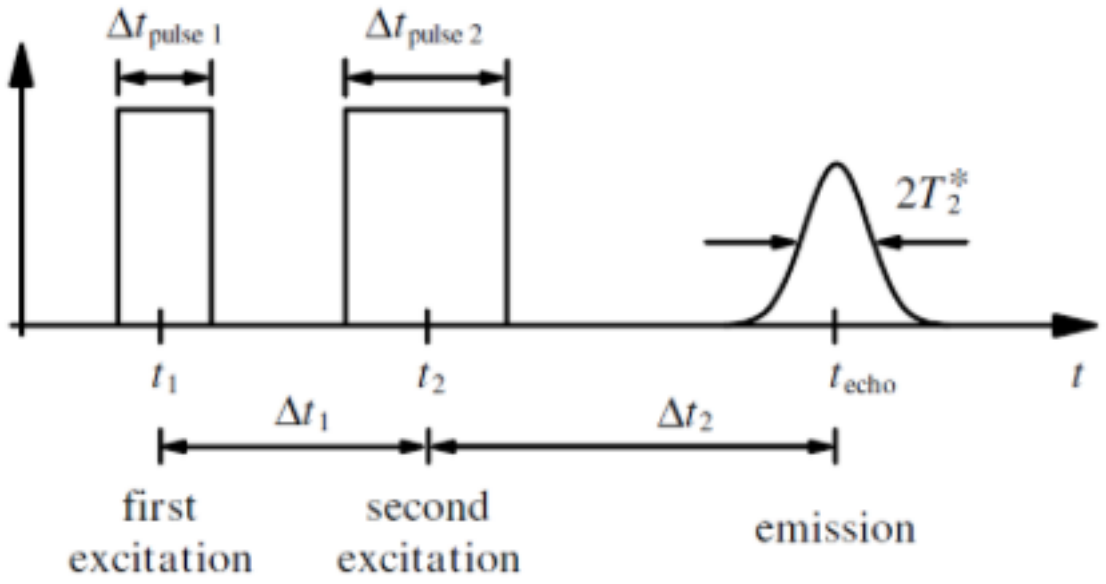
# Photon Echoes

If an ensemble of atoms or molecules is excited with two short and intensive laser pulses of a certain energy with a sufficiently small delay $\Delta t_1$ between them a new pulse can be obtained as a photon echo after a second delay $\Delta t_2$ if several conditions are fulfilled.

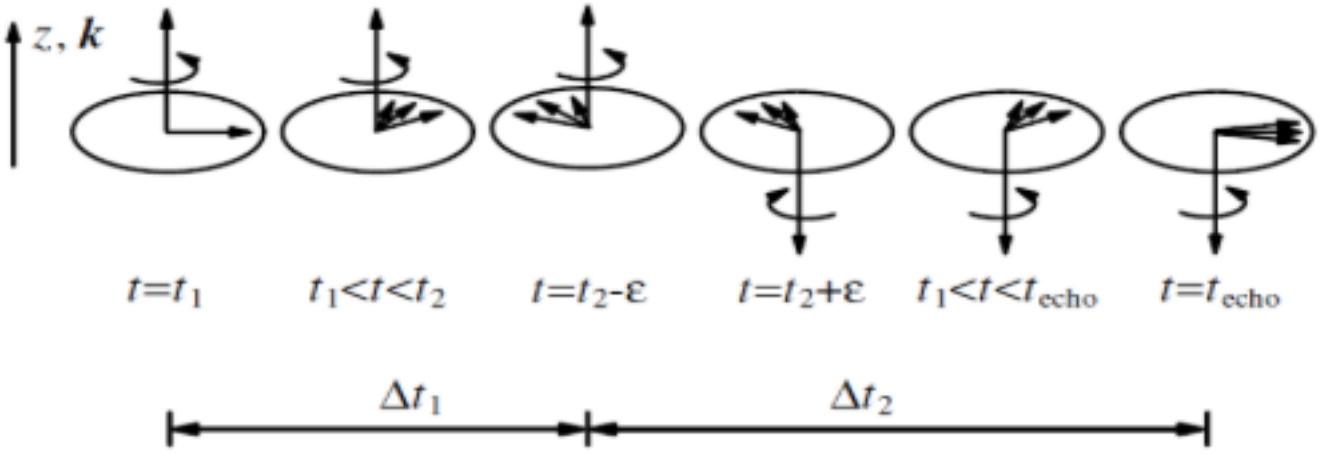
As a result of the excitation with the first short pulse the dipole moments of all particles will first oscillate in phase. However, these particles may have slightly different resonance frequencies distributed over the range $\Delta\nu$ and thus the oscillation will dephase in time.

But for times not longer than T2, the initial phase information is still present in the system. With the second short pulse of a certain energy applied at the time $\Delta t1$ the oscillation can be phase-shifted by $180^\circ$.

As a result the oscillations will rephase and after the time $\Delta t2$ all particles are in phase again except for the phase information loss resulting from T2 collisions. Thus after that time a light pulse can be emitted as an echo of the first two pulses




The phases of the Rabi oscillations may be visualized as given in next Fig. The temporal development of the phases is depicted as the angle of the polar coordinates of the dipole moment vector in the xy plane for an exciting light pulse propagating in the z direction.



If the exciting pulse is short and intensive enough to provide a sufficiently strong electric field: $E_{\mathrm{exc}} \gg \frac{h}{\mu_{ba}} |\nu - \nu_{\mathrm{exc}}|$

- all dipoles will be excited after the pulse with the same phase.
- The phase angle θphase develops in time as:

$$\theta_{\mathrm{phase}} = \int_0^{t_{\mathrm{FWHM,pulse}}} \frac{\mu_{ba}}{2\pi h} E_{\mathrm{exc}} \, \mathrm{d}t.$$

- For the photon echo experiment the first pulse has to produce a phase shift of:

$$1.\ \text{excitation pulse} \quad \theta_{\mathrm{phase,pulse1}} = \frac{\pi}{2}.$$

- During the following time t < t2 the phase angles become more and more different. Usually many oscillations take place. Coherent oscillation is destroyed after the fanning out time T⋆2 :

$$\text{fanning out time} \quad T_2^* = \frac{1}{2\pi\Delta\nu}$$

for the distributed resonance frequencies over the range Δν. T*2 is in photon echo experiments shorter than Δt1/2.

Then a second short intensive laser pulse is applied after a time Δt1. It has to produce a phase shift of:

$$\text{2. excitation pulse} \quad \theta_{\text{phase,pulse2}} = \pi$$

and thus the phase is inverted and the following process can be illustrated as a "back-rotation" in the phase diagram.

Finally after a second time interval Δt2 which is obviously the same as Δt1 = Δt2 all dipoles are in phase again except for the fanning out time resulting from the spectral broadening of the particles. This results in a spreading of the phase and thus the observed emission, the photon echo, of the sample will have a pulse width of 2T*2.

Of course this type of coherence experiment can be carried out only for delay times Δt1/2 shorter than the T2 describing the phase disturbing collisions

---

$$\textbf{photon echo condition} \quad \Delta t_{1/2} < T_2$$

In photon echo experiments phase shifts different from π and π/2 also are possible.

In any case the intensity of the excitation has to be strong enough to produce enough transition dipole moments in competition to the relaxation processes.
Thus the necessary intensities are in the range:

$$\textbf{photon echo intensities} \quad I_{\mathrm{exc}} \geq \frac{c_0 \varepsilon_0 n h}{2\mu_{ba}^2} \left( \frac{1}{T_1} + 2\pi\Delta\nu \right)$$

In addition to temporal and energetic conditions an angular condition for the wave vectors has to be fulfilled:

$$\textbf{wave vector condition} \quad \boldsymbol{k}_{\mathrm{echo}} = 2\boldsymbol{k}_{\mathrm{pulse1}} - \boldsymbol{k}_{\mathrm{pulse2}}$$

# Self-Induced Transparency: 2Π Pulses

If optically thick samples with transmissions in the range of some 10% or below are used in coherent nonlinear experiments the shape of the propagating short pulses will be changed by matter absorption.

It was observed that light pulses of a certain pulse profile (hyperbolic secant) and related pulse energies can transmit even through strongly absorbing samples without any change of their shape and energy.

Such pulses are called 2Π pulses. In this case the front part (leading edge) of the pulse is absorbed producing an inversion in the sample.

This inversion amplifies the trailing part of the pulse and thus the energy is conserved for the pulse. But the process causes a delay of the pulse which is longer the further the pulse transmits through the sample and thus the light seems to move much slower than c0/n.

- The description of this self-induced transparency is based on the nonlinear wave equation (4.7). Assuming the pulse propagates unchanged with velocity vpulse in the z direction through the material with induced dipole moment μmat the temporal part of the wave equation can be written as:

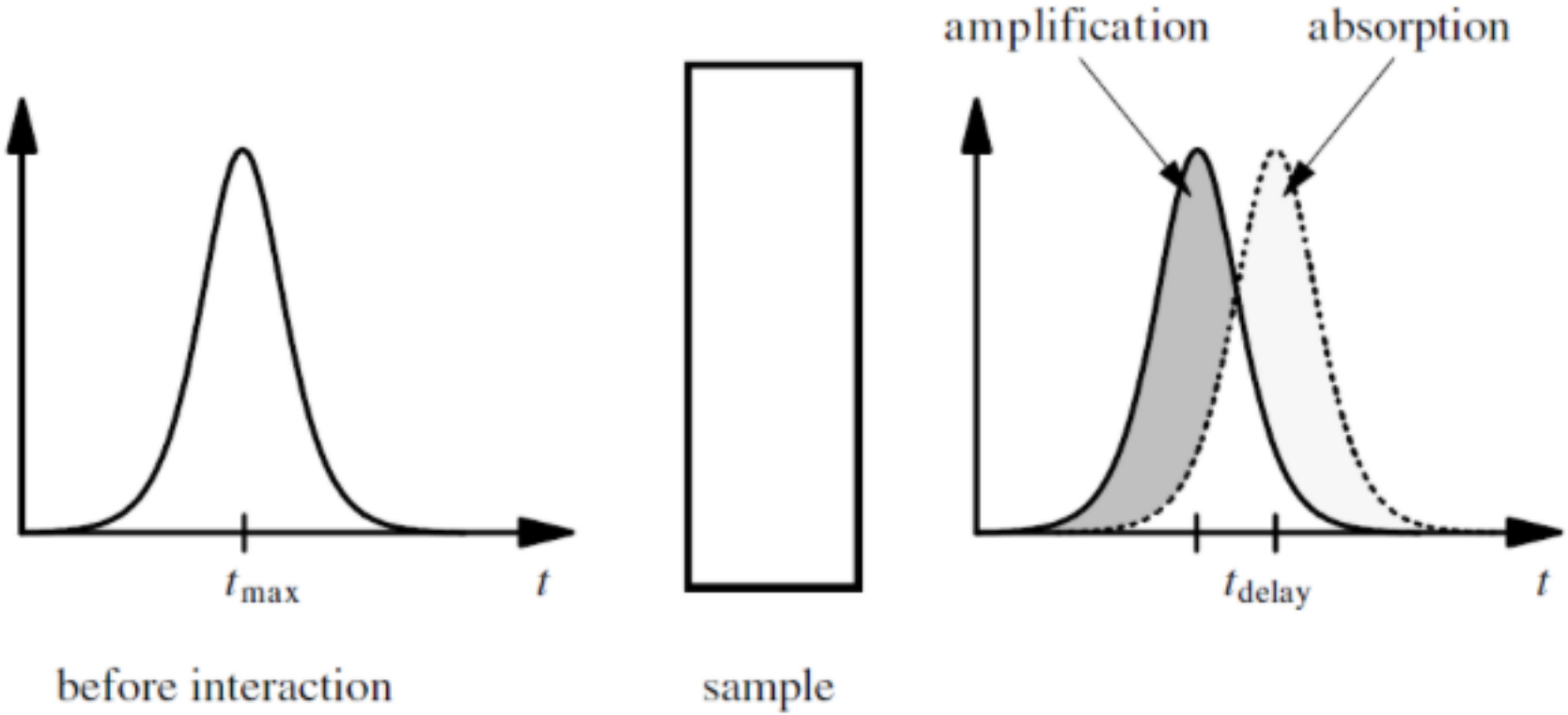
$$\frac{\partial E(t - z/v_{\text{pulse}})}{\partial t} = \frac{1}{\tau_{\text{setr}}} E \sqrt{1 - \left(\frac{2\pi\mu_{ba}\tau_{\text{setr}}}{h} E\right)^2}$$

with

$$\tau_{\text{setr}} = \sqrt{\frac{\varepsilon_0 h}{4\pi c_0 \nu N_0 \mu_{ba}^2} \left(\frac{1}{v_{\text{pulse}}} - \frac{1}{c_0}\right)}.$$

- The solution of this equation gives for the shape of the unchanged pulse:

$$E(t - z/v_{\text{pulse}}) = \frac{h}{2\pi\mu_{ba}\tau_{\text{setr}}} \operatorname{sec\,h}\left[\frac{1}{\tau_{\text{pulse}}}\left(t - \frac{z}{v_{\text{pulse}}}\right)\right]$$




- and the integral over this pulse shape has the value:

$$\int_{-\infty}^{\infty} 2\pi \frac{\mu_{ba}}{h} E \, \mathrm{d}t = 2\pi$$

which explains the name 2Π pulse.

- If the temporal integral of the incident pulse is larger than n times 2π the incident pulse is split into n 2Π pulses. The pulse velocity is approximately given by:

$$\textbf{2}\Pi \textbf{ pulse velocity} \quad v_{\mathrm{pulse}} = \frac{c_0}{1 + 2c_0 a_{\mathrm{mat}} \Delta\nu \tau_{\mathrm{setr}}^2}$$

- with the absorption coefficient amat and the spectral width of the transition Δν.
- Thus the pulse velocity can be reduced by more than a factor of 103 compared to the speed of light and thus time delays

**tdelay = Lsample / vpulse**

of 100 ns or longer can be obtained in samples with lengths Lsample in the cm range

# Superradiance (Superfluorescence)

Coherent coupling of light-emitting particles (without a laser resonator) results in coherent radiation which is called superradiance or superfluorescence.

The resulting intensity **Iradiation** is quadratically proportional to the number of particles as long as no saturation effects occur.

The coherence can be established by coherent excitation of the emitters or it can be based on the sufficient high population of the excited emitting state. Based on spontaneous fluorescence the superradiance can then develop by coherent amplification. Finally a high gain in the material will be obtained.

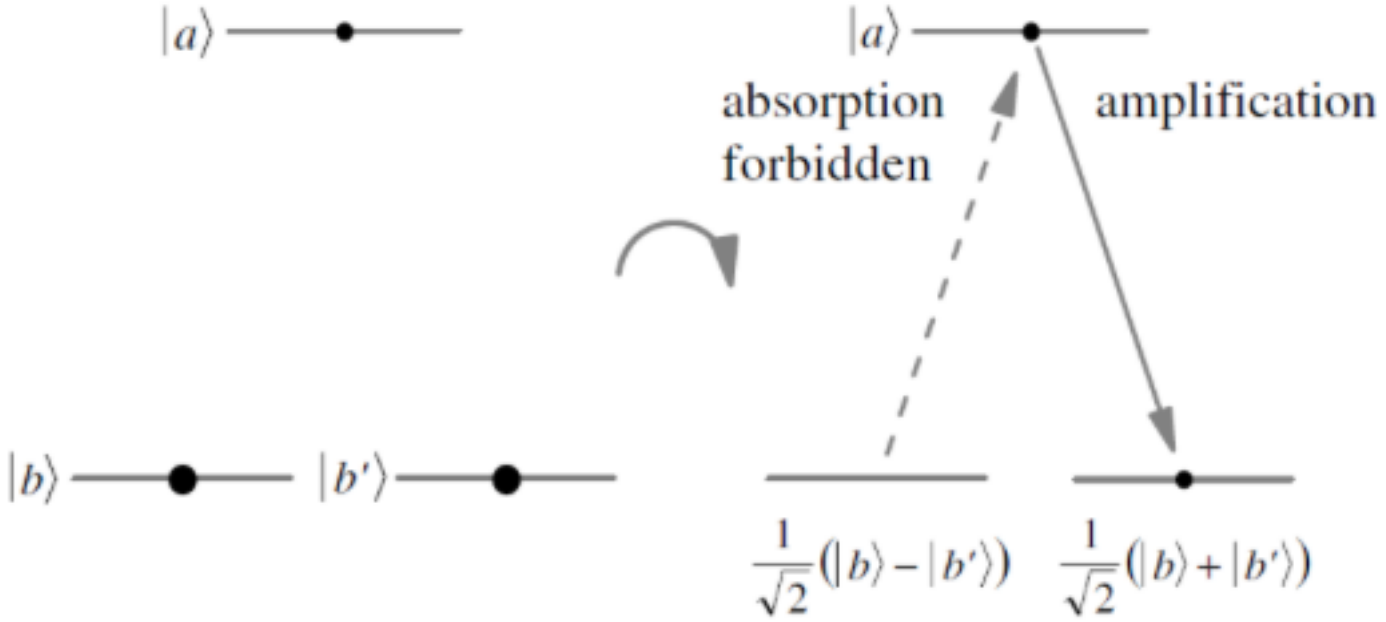
In resonators this superradiance passes to coherent laser radiation.

In excimer and nitrogen lasers the influence of the external resonator is sometimes so small that some of these lasers are named superradiators.

# Amplification Without Inversion

Amplification of light in matter usually demands the inversion of the population densities of the participating energy levels. This inversion is the basic requirement for lasers as usually applied in photonics.

But if three or more energy levels are coherently coupled via the light field the absorption can be decreased in these materials showing a very high refractive index. In some cases even amplification is possible although the population densities are not inverted.



- The lower states $|b\rangle$ and $|b'\rangle$ can be superimposed to the orthogonal states

$$1/\sqrt{2}(|b\rangle - |b'\rangle) \text{ and } 1/\sqrt{2}(|b\rangle + |b'\rangle).$$

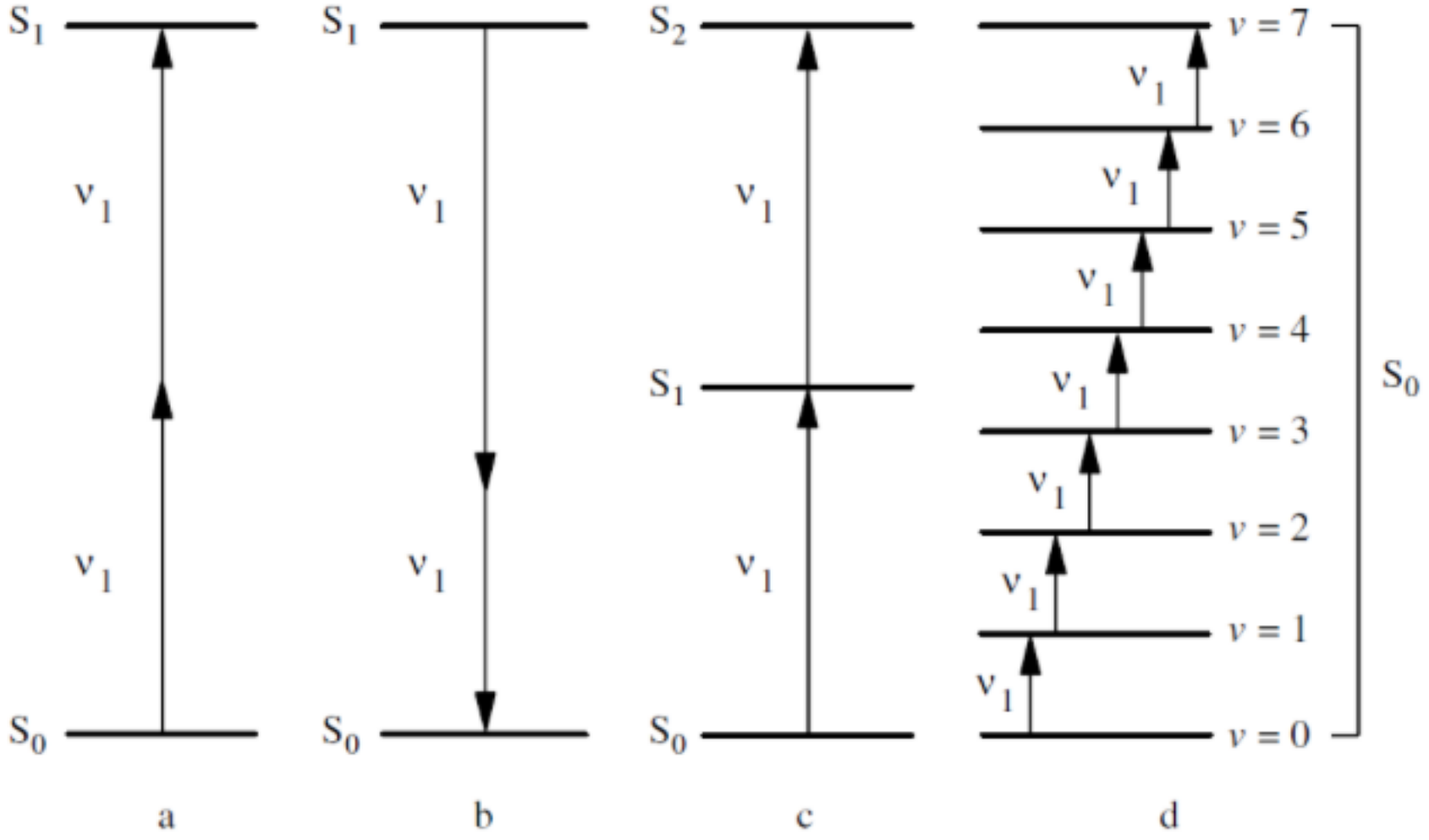
- If the absorption of the first state to the excited state $|a\rangle$ is forbidden it is called a trapped state.

- If most of the particles are in this trapped state and the emission of $|a\rangle$

to the second combined ground state is allow $|a\rangle$ then an $|b\rangle$ ification can be observed without having more particles in than in .

# Two-Photon and Multiphoton Absorption

Absorption and emission of two three or several photons can occur stepwise or simultaneously



As long as the population densities of the involved lower states of the transitions are sufficiently high further absorption to higher states will occur.

But both absorptions via an intermediate energy state or without may occur as coherent interaction between light and the transition dipole moment.

Using rate equations the two-photon transition probability from the state l to the state m can be phenomenological described by:

(1) two-photon absorption from $l$ to $m$ ($N_l \rightarrow N_m$):

$$\frac{\partial N_l}{\partial t} = -\sigma^{(2)}_{l,m} I_1 I_2 N_l \quad \text{and} \quad \frac{\partial N_m}{\partial t} = +\sigma^{(2)}_{l,m} I_1 I_2 N_l$$

(2) two photon emission from $m$ to $l$ ($N_l \leftarrow N_m$):

$$\frac{\partial N_l}{\partial t} = +\sigma^{(2)}_{m,l} I_1 I_2 N_m \quad \text{and} \quad \frac{\partial N_m}{\partial t} = -\sigma^{(2)}_{m,l} I_1 I_2 N_m$$

Usually only small population densities are reached in the excited state and therefore the photon transport equation can then be written as:

$$\frac{\partial I}{\partial z} = -N_{\text{total}} \sigma^{(2)} I_{\text{exc}}^2$$

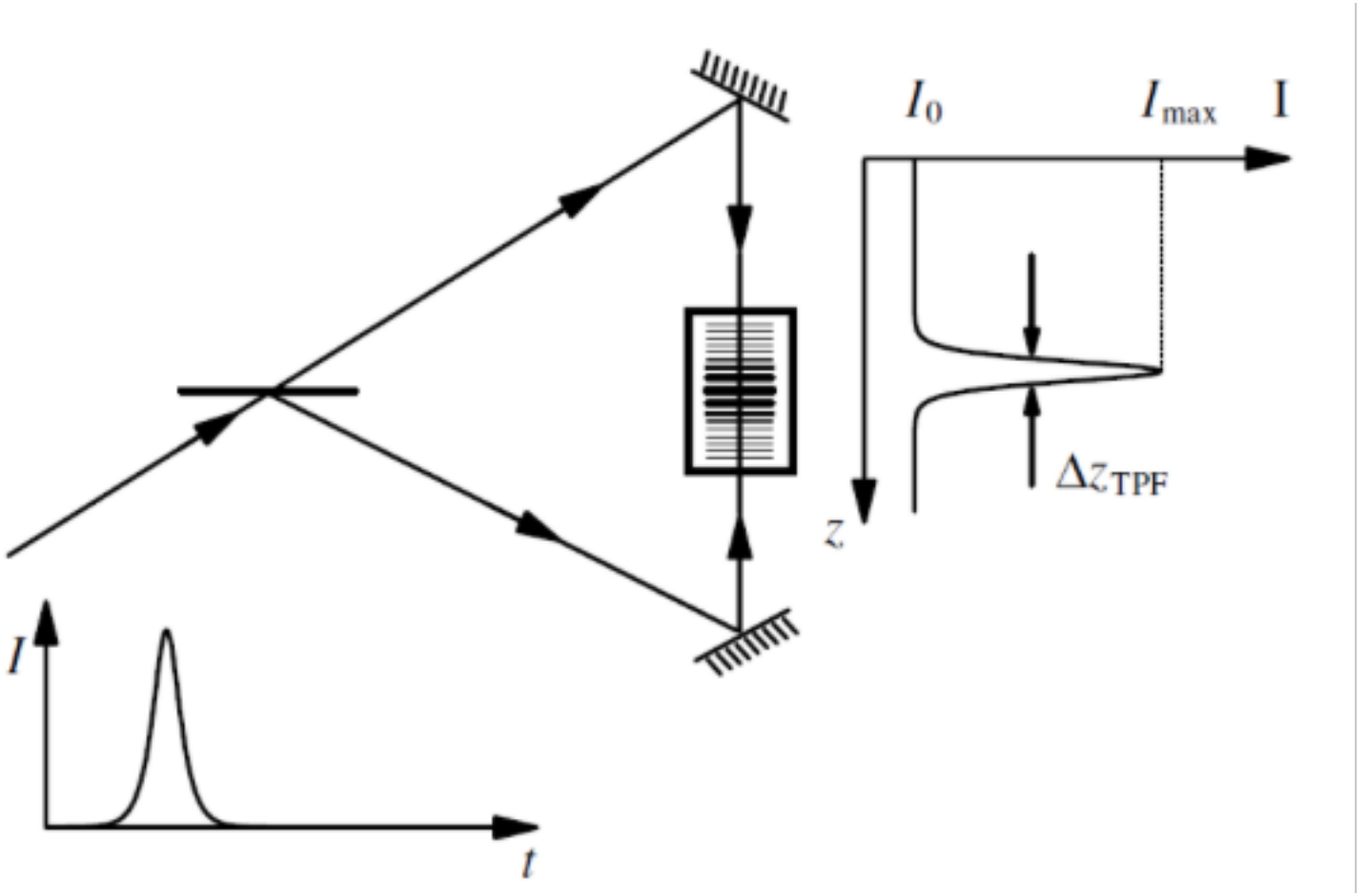
- which can be integrated to give:

$$\textbf{two photon absorption} \quad I(z) = I_0 \frac{1}{1 + \sigma^{(2)} N_{\text{total}} I_0 z}$$

The line shape is for parallel beams the same as the single photon band profile. In the case of two antiparallel beams the broadening effects from the moving particles can be avoided and the resulting two-photon spectra are Doppler-free, allowing, e.g. the resolution of the hyperfine structure of atoms . This can result in strong signals although the two-photon cross-section is much smaller than the single-photon one.

In any case the polarization of the two photons should be the same for the maximum transition probability.

Two photon emission can be stimulated by an incident light beam of frequency ν1 or ν2 and the second photon with frequency ν2 or ν1 respectively will be emitted in the same direction. The spontaneous two photon emission is usually too weak to be observable.




- Conventional fluorescence can be excited via two-photon absorption, called two-photon induced fluorescence (TPF).

This easily to observe secondorder nonlinear process is, together with the above-mentioned applications, also used for the determination of the pulse length of short laser pulses. Two equal shares of an incident beam are guided antiparallel into a cell with strongly fluorescing material (e.g. a laser dye) which can be excited by two-photon absorption with the laser wavelength. In the temporal overlap region of the two pulses the fluorescence will be much stronger over the FWHM range ΔzTPF-FWHM which can easily be measured using a magnifier or a microscope in the sub-mm range. The resulting pulse length in the ps or sub-ps range can be evaluated from:

$$\textbf{pulse width (Gauss)} \quad \Delta t_{\mathrm{FWHM}} = \frac{1}{c\sqrt{2}} \Delta z_{\mathrm{TPF\text{-}FWHM}}$$

with ΔzTPF-FWHM as the full width at half maximum of the TPF signal after background subtraction and the speed of light c in the matter. For hyperbolic secans pulse shapes the pulse width of the exciting signal is smaller for the same spatial width of the TPF signal and follows from:

$$\textbf{pulse width (sech)} \quad \Delta t_{\mathrm{FWHM}} = \frac{1}{1.5429 \cdot c} \Delta z_{\mathrm{TPF\text{-}FWHM}}.$$

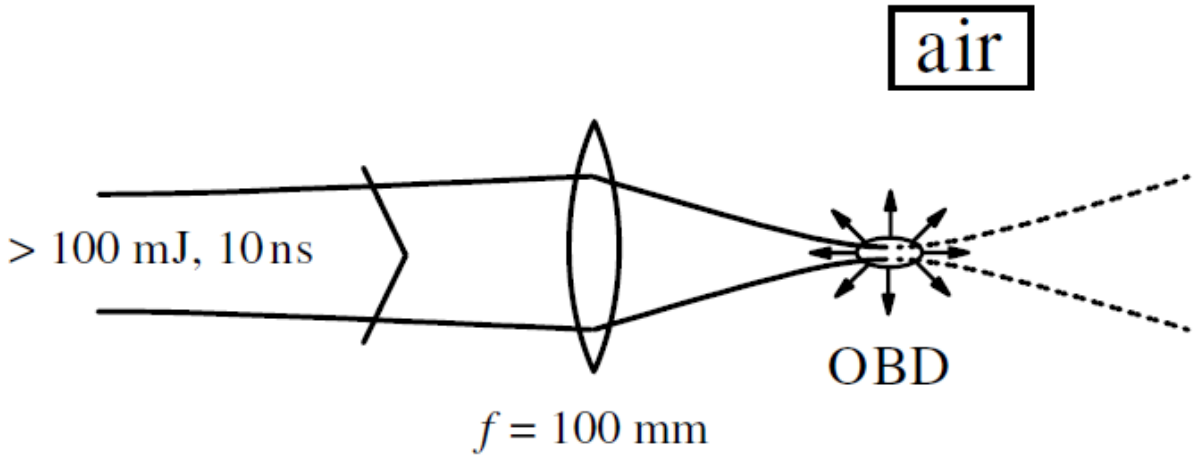
# Photoionization and Optical Breakdown (OBD)

If the intensity is increased to very high values above 1010Wcm−2 s−1 finally all absorbing or nonabsorbing materials can be ionized and possibly damaged. These high intensities can be easily achieved with focusing of short pulses. Besides the effects caused by strong heating

the consequences of the extremely high electric fields and possible photoionization via multiphoton excitation can also be observed. In practical cases mostly a combination of these effects occurs.

If photoionization takes place during a short period many free electrons will be generated and a hot plasma will be obtained. This optical breakdown can be observed, e.g., by focusing a Q switched laser pulse of good beam quality with a few mm diameter, a pulse duration of 10 ns and a pulse energy of 100mJ with a lens with a focal length of 100mm in air .

The obtained "white" light covers a large spectral range as a function of the material and may be used for illumination.




In the generated plasma, optical phase conjugation can occur and thus the laser source can be damaged by the back-scattered light, especially if

oscillator amplifier laser systems are used. In this case optical isolation with a Faraday rotator and a polarizer may be applied to protect the laser source. Multiphoton excitation as discussed in the previous chapter with subsequent ionization leads for the ionization, measured e.g. as the number of generated ions NOBD-ions, as a function of the exciting intensity Iexc to a high-power kOBD: $N_{\text{OBD-ions}} \propto \Delta t_{\text{pulse,FWHM}} I_{\text{exc}}^{k_{\text{OBD}}}$.

The pulse duration ΔtFWHM increases linearly the probability of this ionization.

The exponent kOBD is of the size of the quotient of the ionization energy Eionization divided by the photon energy hνexc:

$$k_{\mathrm{OBD}} \approx \frac{E_{\mathrm{ionization}}}{h\nu_{\mathrm{exc}}}$$

But the observed kOBD values may be smaller. A value of kOBD = 6.5 was observed for the ionization of krypton atoms, which have an ionization energy of 14 eV, with a pulsed ruby laser light of the wavelength of 694 nm.

The theoretical value of kOBD is approximately 10. This discrepancy may be explained by the supporting field emission from the very high electric fields in the light beam and other processes.

Because of the high power of **IkOBD** this effect appears with a threshold character. This "threshold intensity" depends on many parameters.

Impurities can decrease this "threshold" by orders of magnitude. Therefore the "threshold" can be increased by purification if necessary even for "pure" gases by at least one order of magnitude.

# Optical Damage

Damage of optical materials by laser radiation with high powers depends on both the matter and light parameters. Optical damage threshold is different for bulk materials and surfaces.

It is also a function of almost all radiation parameters such as pulse duration, wavelength, intensity and energy, mode structure, beam size and even polarization for nonperpendicular incidence at surfaces.

Most crucial are material impurities such as absorbing, e.g. dust, particles at the surface or in the bulk or inner tensions from the

production process. Optical damage is investigated for optical components such as, e.g. mirrors, laser and frequency converting crystals, coatings and other nonlinear materials.

As a rough guideline the damage intensity Idamage is inversely proportional the square root of the pulse duration Δt.

$$\textbf{pulse width} \quad I_{\text{damage}}(\Delta t) = I_{\text{damage,ref}} \sqrt{\frac{\Delta t_{\text{ref}}}{\Delta t}} + I_{\text{damage,cw}}$$

Sometimes instead of the damage intensity the damage fluence. Fdamage = Idamage Δtpulse is given for a certain pulse width. The damage fluence will increase with the square root of the pulse duration Δtpulse.

$$\textbf{roughness} \quad I_{\text{damage}} \propto \frac{1}{\delta^{m}_{\text{surface}}}$$

Further the damage threshold decreases with increasing spot area Aspot as

$$\textbf{spot size} \quad I_{\text{damage}} \propto \frac{1}{\sqrt{A_{\text{spot}}}}.$$

For absorbing matter the damage threshold decreases with increasing absorption. For absorption coefficients a = −1/L ln T between 0.01 and 50 cm−1 the following formula was observed

$$\text{absorbing matter} \quad I_{\text{damage}} = \frac{264\,\text{kW/cm}^2}{(a/\text{cm}^{-1})^{0.74}}.$$

# Laser Material Processing

In most cases optical material processing is based on the thermal effects of the absorbed light in the matter resulting in characteristic time constants of μs up to seconds.

In general three main types of material processing applications may be distinguished:

• heat treatment (104–105Wcm−2): hardening of steel, surface oxidation;

• melting (105–107Wcm−2): soldering, welding, marking, labeling, cutting,

surface treatment;

• vaporization (107–1010Wcm−2): drilling, cutting, labeling, trimming.

The first two methods can be applied with cw lasers or pulsed systems with pulse widths from ms to ns. The vaporization technique demands pulsed operation in the μs to ps range.

The use of fs laser pulses resulted in drilling and micromachining to very high accuracy and may find applications, too, depending on the price of these lasers and the advantage in precision.

The theoretical description of these material processing applications has to be based on the modeling of the light energy absorption and the following:

Heat distribution in the matter using differential transport equations.

The temperature difference distribution ΔT as a function of the radial distance r and time t inside a sample which is excited at a small spot can be calculated from:

$$\Delta T(r,t) = \Delta E \frac{1}{\rho c_{\mathrm{P}}} (4\pi\kappa t)^{-1.5} \left\{ 1 + \left( \frac{r^2}{\kappa t} - 6 \right) \frac{s^2}{40\kappa t} \right\} \mathrm{e}^{-r^2/4\kappa t}$$

# Combined Interactions with Diffraction and Absorption Changes

The absorption of matter is changed the real part of the refractive index and thus the diffraction will be changed, too. Thus both the amplitude and the phase of the applied light will be changed.

**Change of absorption and refractive index**

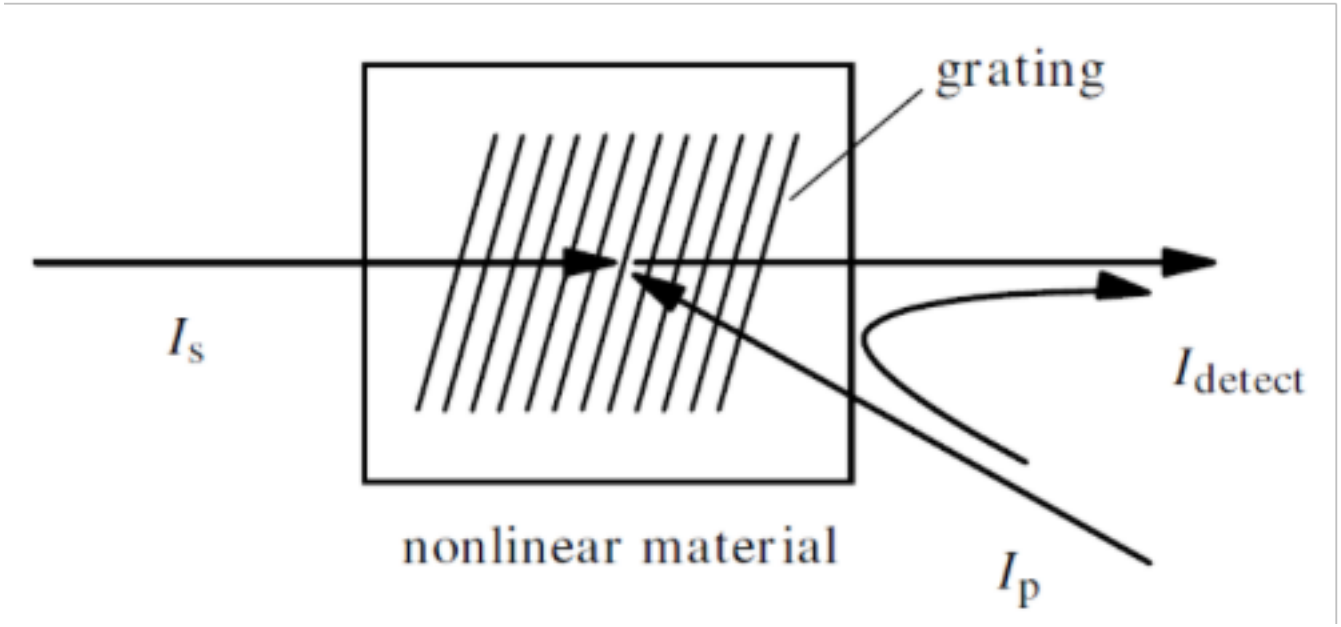
**Change of intensity and phase of the light**

In absorption measurements such as pump and probe techniques the phase change will not always be detected. But if interference setups are used and thus absorption and phase gratings are applied in the matter both changes have to be considered in the interaction of the probe light with the matter.

As the simplest example the generation of transient or permanent gratings by two equal light beams with different propagation directions will be outlined, first.

# Induced Amplitude and Phase Gratings

But here it is assumed here that only two beams are applied :




If, via the nonlinear interaction of the interference pattern from the two beams, an absorption or phase grating is induced in the matter some light of the pump beam p can be diffracted into the direction of the transmitted beam s and vice versa.

If the two beams have distinctively different intensities, an "amplification" of the weaker beam can be obtained. This process is also called two wave mixing (TWM) or beam coupling.

The analysis is easy if the following assumptions about the two beams are justified:

- They are plane waves (e.g. in the waist region of Gaussian beams);
- Coherence is sufficient for complete interference;
- They are linearly polarized perpendicular to the interaction plane;
- Light frequencies are only slightly different;
- Intensities are not to high (below saturation of the nonlinear effect).

The electric fields of the two beams are then given by:

$$E_\mathrm{p} = E_\mathrm{p}^0 \cos(2\pi\nu_\mathrm{p} t - \boldsymbol{k}_\mathrm{p}\cdot\boldsymbol{r} + \varphi_\mathrm{p})$$

and

$$E_\mathrm{s} = E_\mathrm{s}^0 \cos(2\pi\nu_\mathrm{s} t - \boldsymbol{k}_\mathrm{s}\cdot\boldsymbol{r} + \varphi_\mathrm{s})$$

With the resulting intensity modulation in the sample:

$$I_\mathrm{TWM} = I_\mathrm{p} + I_\mathrm{s} + 2\sqrt{I_\mathrm{p} I_\mathrm{s}}\cos\{2\pi(\nu_\mathrm{s} - \nu_\mathrm{p})t - (\boldsymbol{k}_\mathrm{s} - \boldsymbol{k}_\mathrm{p})\cdot\boldsymbol{r} + \Delta\varphi\}$$

and with $\Delta\varphi = \varphi_\mathrm{s} - \varphi_\mathrm{p}$.

The diffraction efficiency of the pump beam with Ip towards the direction of Idetect is a function of the type of grating and the phase difference between Ip and Is

**Table * Diffraction of pump beam Ip towards the direction of Idetect as a function of the relative phase Δϕ between the beams Ip and Is**

| | | | |
|---|---|---|---|
| phase grating | | | |
| $n(z)$: | $\Delta\varphi = 0$ | | $I_{\text{detect}} = \text{min.}$ |
| | $\Delta\varphi = \frac{\pi}{2}$ | | $I_{\text{detect}} = \text{max.}$ |
| amplitude grating | | | |
| $a(z)$: | $\Delta\varphi = 0$ | $I_{\text{detect}} = \text{max.}$ ⇑ bleaching | $I_{\text{detect}} = \text{min.}$ ⇑ induced absorption |
| | $\Delta\varphi = \frac{\pi}{2}$ | $I_{\text{detect}} = \text{min.}$ | |

The maximum diffraction efficiency occurs for refractive index gratings for phase shifts of π/2 between the two beams and for zero phase difference in the case of bleached absorption gratings.

For optimal phases the diffraction efficiency ηdiff , related to the diffracted light can be calculated from:

**diffraction efficiency**

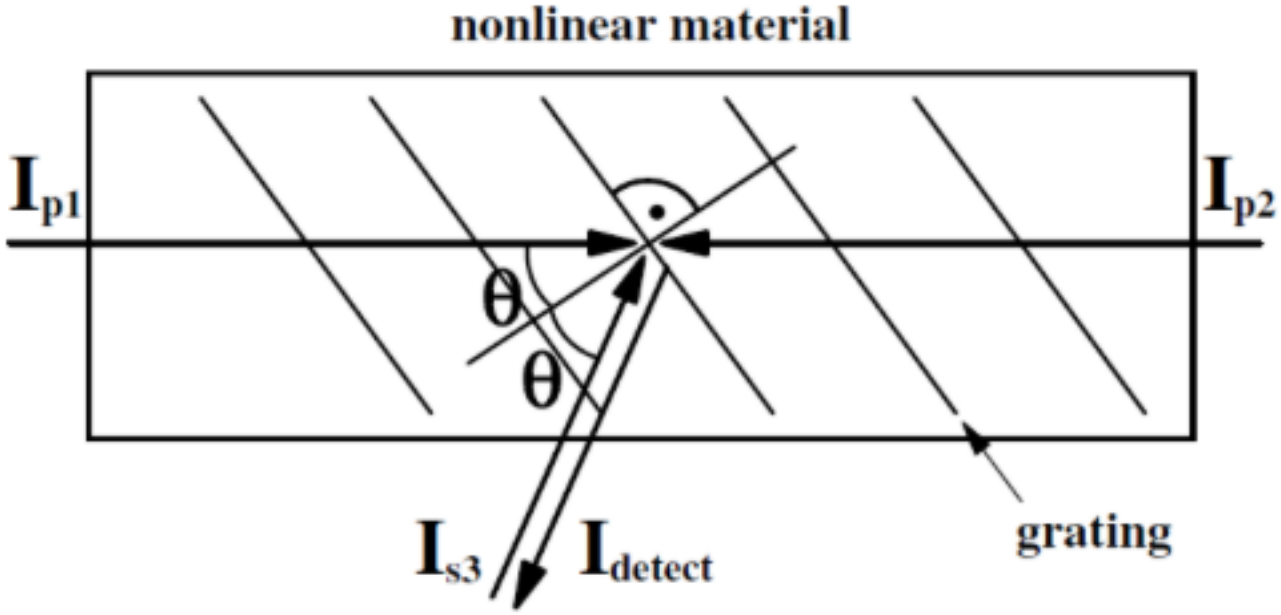
$$\eta_{\text{diff}} = \frac{I_{\text{detect}}}{I_{\text{p}}} = \left(\frac{\pi \Delta n L_{\text{mat}}}{\lambda}\right)^2 + \left(\frac{\Delta \alpha L_{\text{mat}}}{4}\right)^2$$

with the sample thickness Lmat. The maximum change of the refractive index Δn describes the phase grating and the maximum change of the absorption Δa the amplitude grating.:

# Four-Wave Mixing (FWM)

In the four-wave mixing process (FWM) in general two pump beams Ip1 and Ip2 are used to interfere and induce phase or amplitude gratings via a nonlinear optical process together with an additional third beam Is3.

These beams are diffracted at the resulting gratings forming the fourth beam Id4 which is detected. Whereas the grating in conventional holography is static and thus the writing of the grating and the read-out are temporally separated in FWM all processes take place at the same time. Thus FWM is sometimes called real-time or dynamic holography.



This four-wave mixing (FWM) is obviously a third-order nonlinear optical process with nonlinear polarization:

$$\boldsymbol{P}_{\mathrm{nl}}^{\mathrm{FWM}}(\boldsymbol{r},t) = \frac{\varepsilon_0}{2}\chi^{(3)}\boldsymbol{E}_{\mathrm{p1}}(\boldsymbol{r},t)\boldsymbol{E}_{\mathrm{p2}}(\boldsymbol{r},t)\boldsymbol{E}_{\mathrm{s3}}(\boldsymbol{r},t)$$

with a complex third-order susceptibility χ(3) describing phase and amplitude changes of the material as a function of the orientation of the material, the polarization and the frequencies of the light beams with electric fields Ep1, Ep2 and Es3.

Because all beams have to be coherent during the time of interaction in four-wave mixing at least four gratings are induced in the matter.

For example, beam p2 forms a reflection grating with beam s3 as depicted by the grating planes. Beam p1 can be thought of as "reflected" at this grating towards the detection direction of Id4. In addition three more gratings are important in FWM. A reflection

grating results from the interference of the two pump beams p1 and p2.

This grating will have the shortest grating constant and it allows the back reflection of the two pump beams p1 and p2. Another reflection grating is formed by s3 and d4. The fourth is a transmission grating generated by the beams p1 and s3 as well as by p2 and d4 .

Grating planes will always occur in the direction of the half-angle plane between the beams.

Energy and momentum conservation have to be fulfilled for the photons in the FWM scattering process and therefore

$$\nu_{\mathrm{p1}} + \nu_{\mathrm{p2}} = \nu_{\mathrm{s3}} + \nu_{\mathrm{detect}}$$

and

$$\boldsymbol{k}_{\mathrm{p1}} + \boldsymbol{k}_{\mathrm{p2}} = \boldsymbol{k}_{\mathrm{s3}} + \boldsymbol{k}_{\mathrm{detect}}$$

are required.

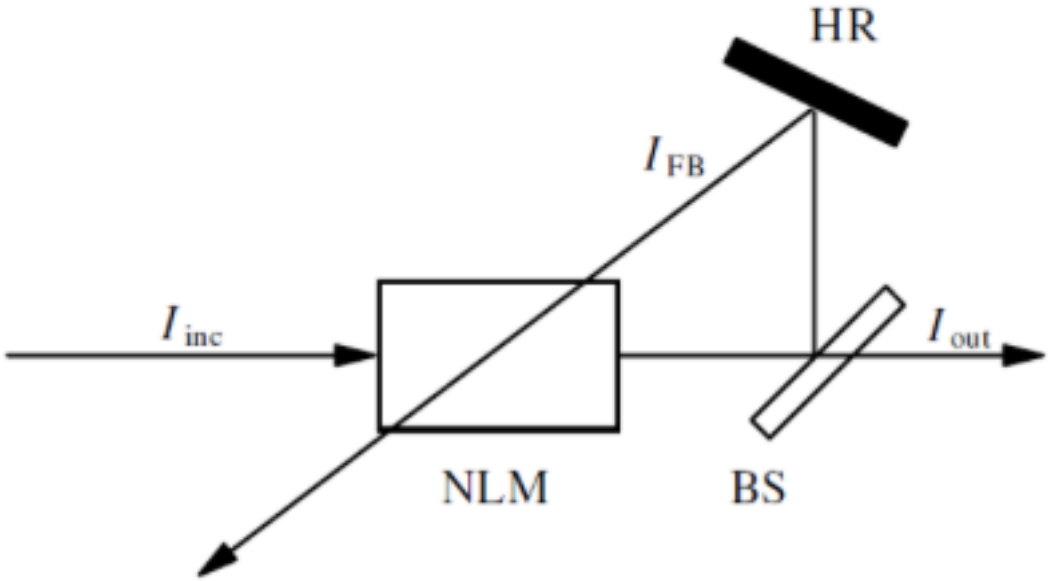
If the signal beam with intensity Is3 is equal to one of the pump beams

four-wave mixing is observed as a two-wave mixing process (TWM)

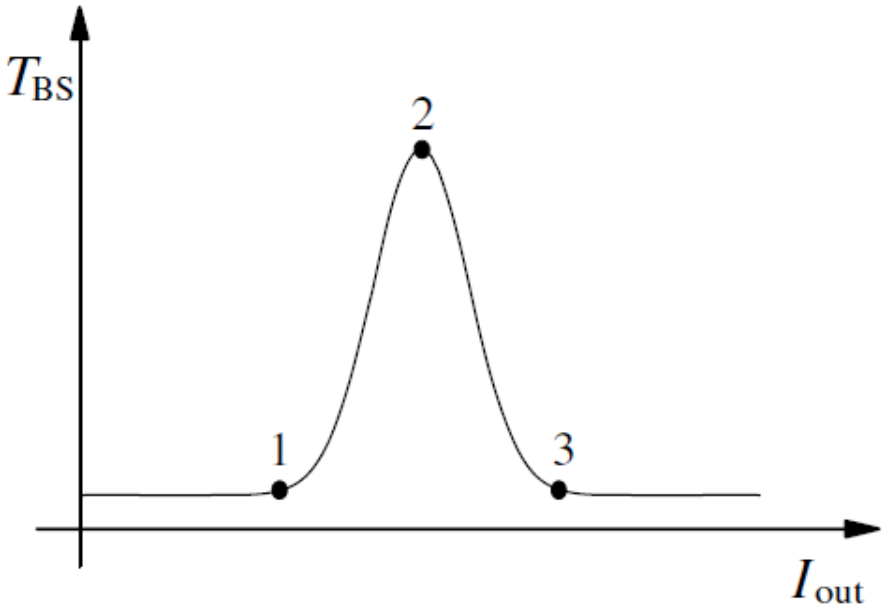
# Optical Bistability

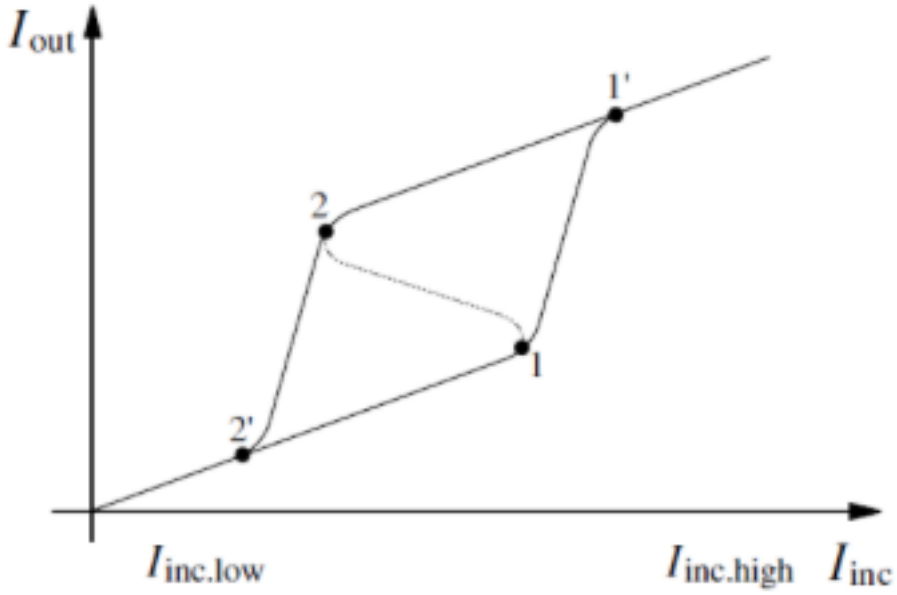
Optical bistability is exhibited by optical devices which show ideally two stable transmission values T1 and T2 as a function of the input beam parameters, especially its intensity. These devices can be used for optical switching. Achieving optical bistability requires an optical nonlinear element and optical feedback.

The transmission Tbs of the material is then given as a function of the output intensity Tbs = T(Iout).




If this is, e.g. a bell-shaped function the output intensity Iout as a function of the incident intensity Iinc will reflect this behavior in a nonmonotonic shape.



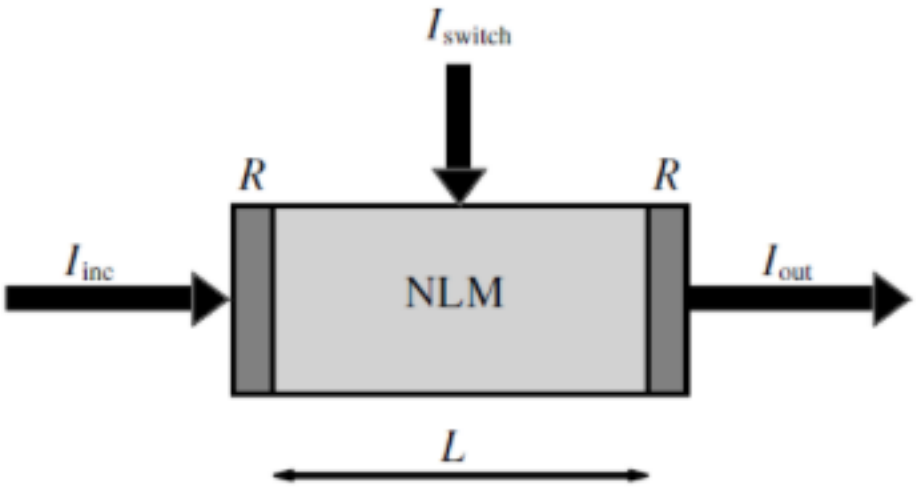




- This results in an ambiguous function of the output intensity as a function of the incident intensity which crosses an unstable region between points 1 and 2. Thus the output intensity will jump from point 1 to point 1' if the input intensity is increased and from point 2 to point 2' if the input intensity is decreased.
- At these points the transmission is changed rapidly. Thus the device should be used for incident intensities between Iinc, low and Iinc, high. Many kinds of nonlinear effect can be applied for such bistable optical devices. As an example a nonlinear absorber inside a Fabry–Perot interferometer can be used for this optical bistability shape.

as a simple approach to describe the nonlinear transmission of the sample by the low signal absorption coefficient a0 and the nonlinear intensity Inl the transmission of this bistable device can be written as:.

$$T(I_{\text{out}}) = \frac{I_{\text{out}}}{I_{\text{inc}}} = \left[1 + \frac{a_0 L}{(1-R)(1+2I_{\text{out}}/I_{\text{nl}})}\right]^{-2}$$

If both the reflectivity R of the Fabry–Perot mirrors and the transmission T of the material are close to one. In this formula L is the length of the active material.




The operation of this device is better the higher the quotient (1−T)/(1−R). Besides nonlinear absorption the nonlinear Kerr effect can also be applied for optical bistability. If the Kerr material is used as the nonlinear material, the nonlinear transmission of the device can be written as

$$T(I_{\text{out}}) = \frac{(1-R)^2}{(1-R)^2 + 4R\sin^2[2\pi L/\lambda_0(n + 2\gamma_I I_{\text{out}}(1-R))]}$$

# Materials in Resonant Nonlinear Optics

Potentially many kinds of gases, liquids, solutions and solids are useful for nonlinear optical applications based on nonlinear absorption and emission.

Most important are laser materials which are described in the next chapter. Also important are nonlinear absorbers applied for Q switching and mode locking in laser oscillators.

Organic and inorganic systems such as solids or liquids are used for this purpose.

Optical switching, storage and especially new display technologies may become even more important in the next few years. For these applications better knowledge about the nonlinear optical processes and the quantum mechanical structure of these functions is demanded.

# Organic Molecules

The parameters of molecular systems can vary in wide ranges:

- spectral absorption bands: UV-Vis-IR (150 nm–10 μm);
- cross-sections (molecules): < 10−15 cm2;
- cross-sections (aggregates): > 10−15 cm2;
- lifetimes: fs – years;
- saturation intensities: < kWcm−2 → GWcm−2.

Organic matter is used in photonics, e.g. as a laser material (e.g. dye lasers), as an optical switch (e.g. Q switch and mode locker) and as a waveguide. Potential applications may be new emitters for new displays (e.g. OLEDs) or for new lasers, advanced optical switching and optical storage, nonlinear phototherapy in medicine and new solar energy techniques.

# Anorganic Crystals

In principle all laser materials can be used as nonlinear optical switches or for other photonic applications, too.

For Q switching the absorption wavelength has to fit the emission wavelength of the active laser material and the absorption cross-section has to be larger than the emission cross-section of the laser material

# Photorefractive Materials

Photorefractive materials can show strong nonlinear optical effects at low intensities based on local charge displacement followed by a refractive index change. typical time constants are in the range of ms up to minutes. These materials are typically used with only very small absorption at the applied wavelength which increases the nonlinear reaction.

Therefore the photorefractive material is illuminated with an excitation intensity grating leading finally to a refractive index grating. At this

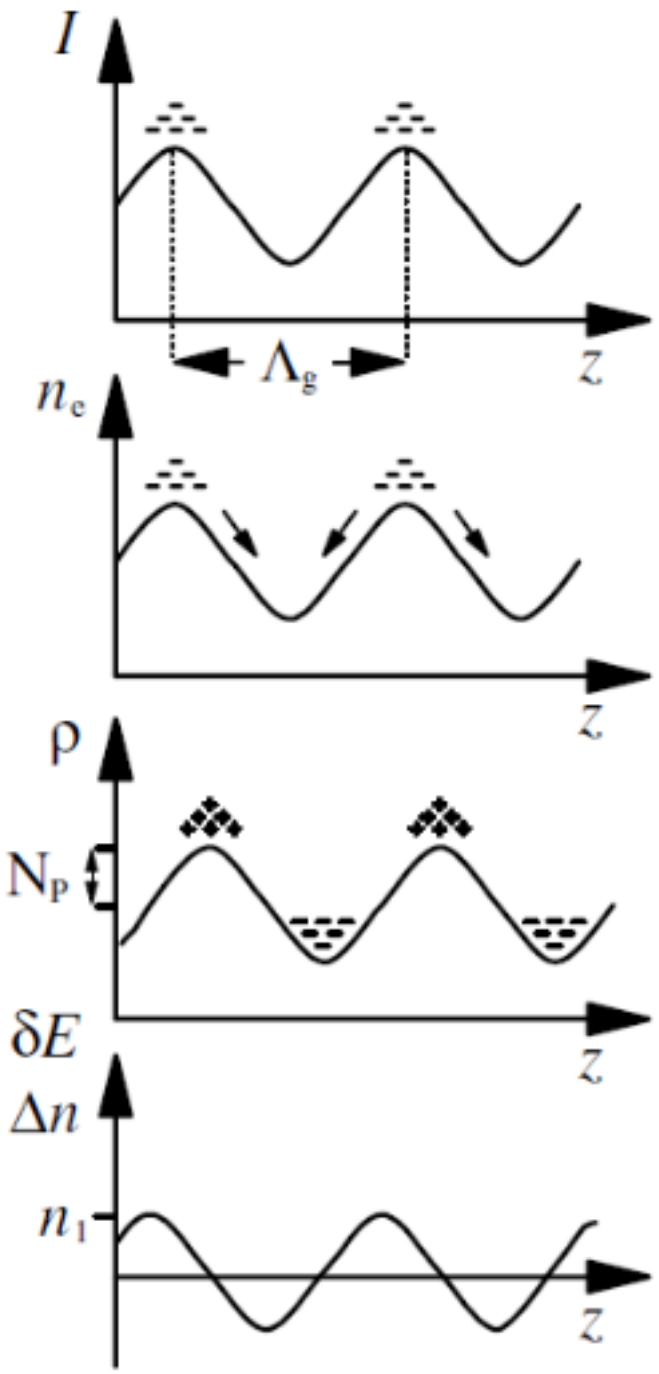
This process takes place in four steps. These steps are:

(i) The excitation intensity grating I(z) over the spatial coordinate z with the grating constant $\Lambda g$ as a result of light interference of two pump beams produces charge carriers in the illuminated areas proportional to the excitation intensity.

(ii) These electrons with density ne, migrate due to electrostatic forces via drift and diffusion to the less illuminated, dark areas.

(iii) The photovoltaic effect produces a space charge separation of $\rho$ with density of photoexcitations Np.

(iv) The resulting difference of the electric field $\delta E$ leads to a modulation of the refractive index $\Delta n$ in the matter with the amplitude n1.




- The minimum time constant τphotoref for obtaining the index changes is a function of the intensity Iexc, the absorption coefficient amat and the desired density of photoexcitations Np:

$$\text{buildup time} \quad \tau_{\text{photoref}} \geq \frac{N_p}{a_{\text{mat}} I_{\text{exc}}}$$

- where it is assumed that the decay of the space charge separation is much longer than the buildup and therefore an integration occurs.
- The density of photoexcitations Np yields the modulation depth n2 of the refractive index n0 of the material:

$$\text{index modulation} \quad n_2 = \frac{1}{4} n_0 r_{\text{eo}} \frac{N_p \eta_{\text{photoexc}} e_e}{\varepsilon} \Lambda_g$$

# Semiconductors

Besides the rapidly increasing importance of semiconductors in diode lasers. They are also used as optical nonlinear devices.

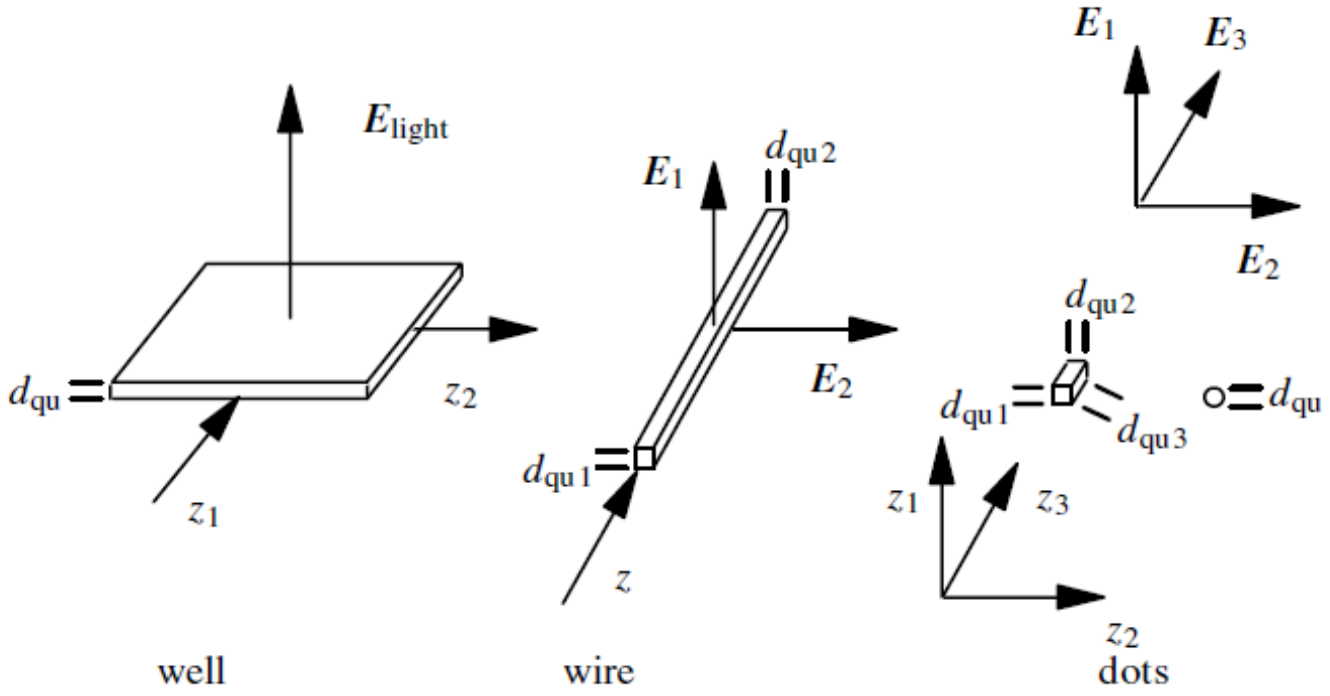
High cross-sections of up to 5· 10−19 cm2 as well as high carrier concentrations of up to 1022 cm3 are possible. Lifetimes can be as short as ns.

The possibility of shifting the long-wavelength absorption band edge from the visible to near infrared wavelengths by varying the concentration of suitable mixtures make them adaptable to desired applications.

# Nanometer Structures

Geometrical structures with dimensions in the nm range and thus less than the light wavelength can show strong absorption in the UV-Vis-NIR spectral range.

The small dimension can be realized in one dimension resulting in a quantum well in two dimensionsm, which is a quantum wire and in all three dimensions representing a quantum dot.



Such nm-structures can be designed in many ways and they can have good optical stability. They can be built with different semiconductors or metals.

The surface can be covered with organic and inorganic matter based on thin films and thus the optical properties can be changed over wide ranges.