Chapter 7
Nonlinear Absorption and Refraction of Light

Nonlinear light absorption is a basic phenomenon of the interaction between the light and the matter. The nonlinear absorption can be described as the absorption coefficient of the medium being a function of the light intensity. Firstly this chapter studies the single-photon absorption (SPA) and the two-photon absorption (TPA) based on the light-matter interaction under the condition of far away the resonance. Secondly this chapter studies the saturable absorption (SA) and the reverse saturable absorption (RSA) based on the light-matter interaction under the condition of close to the resonance. In addition, the applications of these nonlinear absorptions are also introduced, such as the application of TPA in the semiconductor all-optical switches and the application of RSA in the all-optical limiters. In this chapter, according to the K–K relation, we also discuss the single-photon refraction (SPR) related to the single-photon absorption (SPA); the saturable refraction (SR) and the reverse saturable refraction (RSR) related to the SA and the RSA, respectively.

7.1 Single-Photon Absorption and Two-Photon Absorption

7.1.1 Light-Intensity Transmission Equations

1. **Light-Intensity Transmission Equations for SPA and/or TPA**

When a laser beam propagates in a medium, if the interaction between light and matter is far away from the resonance, it may exists two kinds of absorptions in the medium at the same time: the single-photon absorption and the two-photon absorption. We denote the total absorption coefficient of medium as α_T:

$$\alpha_T = \alpha + \beta I. \tag{7.1.1}$$

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where α is the single-photon absorption coefficient, I is the light intensity, and β is a ratio coefficient, it is called the two-photon absorption coefficient.

Suppose a laser beam with intensity I and at frequency ω propagates along z-axis direction in the medium. Because of the existence of light absorption, the light intensity decreases with the increase of the transmission distance. The light-intensity transmission equation can be expressed as

$$\frac{dI}{dz} = -\alpha_{\mathrm{T}} I = -(\alpha + \beta I)I. \tag{7.1.2}$$

The numerical value of β is generally very small. When the light intensity is not very strong, i.e., $\alpha >> \beta I$, the TPA can be neglected, so the Eq. (7.1.2) can be written as

$$\frac{dI}{dz} = -\alpha I. \tag{7.1.3}$$

This is the light-intensity transmission equation for the single-photon absorption in $\alpha >> \beta I$ case.

However, if the light intensity I being strong enough to lead $\beta I >> \alpha$, the single-photon absorption coefficient can be neglected, i.e., $\alpha \approx 0$, Eq. (7.1.2) can be written as

$$\frac{dI}{dz} = -\beta I^2. \tag{7.1.4}$$

This is the light-intensity transmission equation for two-photon absorption process in $\beta I >> \alpha$ case.

As we know that the medium is composed by atoms or molecules. Supposing the energy-level structure of the atom or molecule is a two-level system, and denoting the lower energy level as E_1 and the upper energy level as E_2, when a light inputs the medium, the atoms or molecules could absorb the incident photons to make the energy-level transition in the certain condition. If the photon energy $\hbar\omega$ is near the energy difference between two levels, i.e., $\hbar\omega = E_2 - E_1$, in this case the SPA is dominator. However, if the photon energy $\hbar\omega$ is near a half of the energy difference between two levels, i.e., $\hbar\omega = (E_2 - E_1)/2$, in this case the TPA is dominator. It can be seen that the light absorption of medium is whether SPA or TPA depends on the frequency of the incident light and the energy-level structure of medium.

From the light-intensity transmission Eq. (7.1.2) we can see that the light absorption is whether SPA or TPA also depends on the light intensity I: in weak light intensity case the absorption is appeared SPA; but in strong light intensity case the absorption is appeared TPA. As we know that the light intensity is $I = (N\hbar\omega)/\Delta S \Delta t$, where N$\hbar\omega$ is the total light energy ($\hbar\omega$ is the energy of photon, N is total photon number), ΔS is the cross sectional area of passing light and Δt is the time of passing light (near the pulsewidth of light). So the intensity I is inversely proportional to the pulsewidth of light Δt, For example, the pulsewidth of femtosecond laser is shorter than that of picosecond laser in1000 times, so the intensity of the femtosecond laser is larger than that of picosecond laser in 1000 times. Therefore, under the action of the picosecond (or wider) pulsed laser, the absorption performance of the medium belongs to the SPA. Nevertheless under the action of femtosecond laser, the medium shows the TPA effect. In short, the light absorption performance of the medium also relies on the pulsewidth of the incident light.

2. Light-Intensity Transmission Equations in Third-Order Nonlinear and Linear Case

If we only consider the third-order nonlinear optics effect in off-resonance case, the single-photon absorption coefficient can be expressed as

$$\alpha = \alpha_0 + \Delta\alpha = \alpha_0 + \alpha_2 I, \tag{7.1.5}$$

where α_0 is the linear absorption coefficient, $\Delta\alpha$ denotes the third-order nonlinear absorption in SPA process, which is proportional to the light intensity I, α_2 is a ratio coefficient, it is called the nonlinear absorption coefficient. In the next section we will show that $\Delta\alpha$ is negative, i.e., $\alpha_2 < 0$, so the single-photon absorption coefficient α can be expressed as

$$\alpha = \alpha_0 - |\alpha_2| I. \tag{7.1.6}$$

Equation (7.1.6) shows that the absorption coefficient α is a linear function of the light intensity I, and the single-photon absorption coefficient decreases with the increase of the intensity.

As we mention before, the two-photon absorption βI is proportional to the light intensity I, same as the third-order nonlinear absorption $\alpha_2 I$ in SPA, so TPA is also a kind of third-order-nonlinear effects. But the sign symbols of both ratio coefficients are different: $\beta > 0$ and $\alpha_2 < 0$. The total nonlinear absorption can be written as

$$\alpha_{\mathrm{T}} = \alpha + \beta I = \alpha_0 - |\alpha_2| I + \beta I. \tag{7.1.7}$$

Substituting Eq. (7.1.7) into Eq. (7.1.2), then we obtain:

$$\frac{dI}{dt} = -\alpha_0 I - (\beta - |\alpha_2|) I^2. \tag{7.1.8}$$

This is the light-intensity transmission equation when considering the third-order nonlinear effects of SPA and TPA.

Actually, in general $|\alpha_2|$ is much smaller than β, i.e., $\beta > > |\alpha_2|$, so that the light-intensity transmission equation can be approximately written as

$$\frac{dI}{dz} = -\alpha_0 I - \beta I^2. \tag{7.1.9}$$

This is the light-intensity transmission equation when omitting the single-photon nonlinear absorption.

Equation (7.1.9) shows that when the incident-light intensity is very small, all of the nonlinear effects can be ignored, thus Eq. (7.1.9) becomes

$$\frac{dI}{dz} = -\alpha_0 I. \tag{7.1.10}$$

This is the light-intensity transmission equation for the single-photon absorption in low-intensity case.

7.1.2 Single-Photon Nonlinear Absorption and Refraction

1. Single-Photon Nonlinear Absorption

If a monochromatic light at frequency ω is inputted into an isotropic medium with thickness of L, and it propagates along the z-coordinate direction, denoting the light-field amplitude at z point as $\boldsymbol{E}(z,\omega)$, the light intensity at that point as $I(z,\omega)$, the inputted field amplitude as $\boldsymbol{E}(0,\omega)$ and the outputted field amplitude as $\boldsymbol{E}(L,\omega)$, consequently the third-order nonlinear single-photon absorption process is shown in Fig. 7.1, where the total absorption coefficient of medium α can be divided into two parts: the linear absorption α_0 and the nonlinear absorption $\Delta\alpha$.

As we know that the steady-state nonlinear wave equation in the isotropic medium under the slowly-varying-amplitude approximation is

$$\frac{d\boldsymbol{E}(z,\omega)}{dz} = \frac{i\omega}{2\varepsilon_0 c n_0}\boldsymbol{P}(z,\omega). \tag{7.1.11}$$

We only consider the first- and third-order nonlinear polarization processes, the total polarization is given by

$$\boldsymbol{P}(z,\omega) = \boldsymbol{P}^{(1)}(z,\omega) + \boldsymbol{P}^{(3)}(z,\omega). \tag{7.1.12}$$

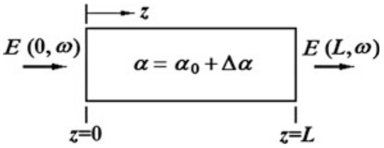


Fig. 7.1 Schematic diagram of the third-order nonlinear single-photon absorption process

Because we just discussed the light absorption, only taking the imaginary part of susceptibility $i\chi''$, the first-order linear polarization is

$$\boldsymbol{P}^{(1)}(z,\omega) = i\varepsilon_0\chi^{(1)''}(\omega)\boldsymbol{E}(z,\omega). \tag{7.1.13}$$

And the third-order nonlinear polarization is

$$\boldsymbol{P}^{(3)}(z,\omega) = 3i\varepsilon_0\chi^{(3)''}(\omega;\omega,-\omega,\omega)|\boldsymbol{E}|^2\boldsymbol{E}(z,\omega). \tag{7.1.14}$$

Substituting Eqs. (7.1.12)–(7.1.14) into Eq. (7.1.11), we will obtain

$$\frac{d\boldsymbol{E}(z,\omega)}{dz} = -\frac{1}{2}\left[\frac{\omega}{cn_0}\chi^{(1)''}(\omega) + \frac{3\omega}{cn_0}\chi^{(3)''}(\omega;\omega,-\omega,\omega)|\boldsymbol{E}|^2\right]\boldsymbol{E}(z,\omega). \tag{7.1.15}$$

Using $I = \frac{1}{2}\varepsilon_0 cn_0|\boldsymbol{E}|^2(\omega)$, Eq. (7.1.15) becomes

$$\frac{d\boldsymbol{E}(z,\omega)}{dz} = -\frac{1}{2}\left[\frac{\omega}{cn_0}\chi^{(1)''}(\omega) + \frac{6\omega}{\varepsilon_0 c^2 n_0^2}\chi^{(3)''}(\omega)I\right]\boldsymbol{E}(z,\omega). \tag{7.1.16}$$

We express the first item of the right side of Eq. (7.1.16) as the linear absorption coefficient α_0:

$$\alpha_0 = \frac{\omega}{cn_0}\chi^{(1)''}(\omega), \tag{7.1.17}$$

and the second item is the nonlinear absorption coefficient $\Delta\alpha$:

$$\Delta\alpha = \frac{6\omega}{\varepsilon_0 c^2 n_0^2}\chi^{(3)''}(\omega)I, \tag{7.1.18}$$

the total absorption coefficient α is then

$$\alpha = \alpha_0 + \Delta\alpha. \tag{7.1.19}$$

To replace the bracket in Eq. (7.1.16) with Eq. (7.1.19), then we will obtain the integral solution of the field amplitude at z point:

$$\boldsymbol{E}(z,\omega) = \boldsymbol{E}(0,\omega)e^{-\frac{\alpha}{2}z}. \tag{7.1.20}$$

Therefore, the relationship between the input intensity and the output intensity is

$$I(z) = I(0)e^{-\alpha z}. \tag{7.1.21}$$

This means that for a certain input intensity $I(0)$ and medium absorption coefficient α, the output intensity presents an exponential decay with the increase of z.

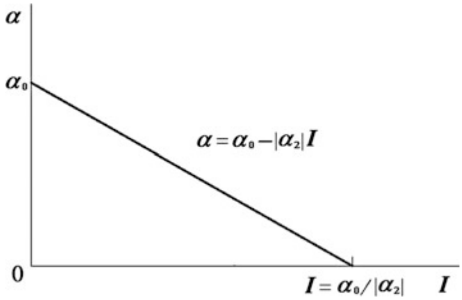


Fig. 7.2 The absorption coefficient of medium as a function of the intensity in the case of third-order nonlinear polarization for the single-photon absorption

According to Eqs. (7.1.19) and (7.1.18), the absorption coefficient α in Eq. (7.1.21) can be expressed as

$$\alpha = \alpha_0 + \Delta\alpha = \alpha_0 + \alpha_2 I. \tag{7.1.22}$$

where α_2 is the nonlinear absorption coefficient, which can be written as

$$\alpha_2 = \frac{6\omega}{\varepsilon_0 c^2 n_0^2}\chi^{(3)''}(\omega). \tag{7.1.23}$$

Obviously, α_2 is proportional to the imaginary part of the third-order susceptibility. It can be proved that $\chi^{(3)''}(\omega) < 0$, so $\alpha_2 < 0$, Eq. (7.1.22) can be written as

$$\alpha = \alpha_0 - |\alpha_2| I. \tag{7.1.24}$$

Equation (7.1.24) means that the absorption coefficient linearly decreases with the increase of light intensity. When $I = \alpha_0/|\alpha_2|, \alpha = 0$, the curve of α verses the I is shown in Fig. 7.2.

Assuming the length of the medium is L, the transmittance of medium can be expressed as

$$T = \frac{I(L)}{I(0)} = e^{-\alpha L} = e^{-(\alpha_0 - |\alpha_2| I)L}. \tag{7.1.25}$$

In this case the transmittance of medium increases with the increase of intensity. When $I \to \alpha_0/|\alpha_2|, T = 1$. That means in the high-power case the medium becomes transparency without absorption.

2. Single-Photon Nonlinear Refraction

According to the K–K relation [see Eq. (2.3.32)], there is a relationship between the refractive-index change and the absorption coefficient change, which is

$$\Delta n(\omega) = \frac{c}{\pi} P \cdot V \cdot \int_0^{\infty} \frac{\Delta\alpha(\omega')}{\omega'^2 - \omega^2} d\omega'. \tag{7.1.26}$$

One can conduct an experiment to test the $\Delta\alpha = \alpha - \alpha_0$ for different frequency to get a $\Delta\alpha(\omega')$ spectrum, and calculate by using Eq. (7.1.26) to get $\Delta n = n - n_0$ for a certain ω, where n_0 is the linear absorption coefficient. Therefore the nonlinear refractive index of medium n for a certain ω can be obtained.

As we know that when an incident laser at ω and with I inputs into the medium, the Kerr effect will happen:

$$n = n_0 + \Delta n = n_0 + n_2 I. \tag{7.1.27}$$

where n_2 is the nonlinear absorption coefficient. Equation (7.1.27) tells us that the refractive index of medium n is a function of the intensity I, this is just the third-order nonlinear refraction in the single photon case.

We have learnt from Chaps. 2 to 5 that the n_2 is proportional to the real part of the third-order susceptibility:

$$n_2 = \frac{3}{\varepsilon_0 c n_0^2} \chi^{(3)\prime}(\omega). \tag{7.1.28}$$

We can see that Eqs. (7.1.27) and (7.1.28) for describing the nonlinear refraction are corresponding to Eqs. (7.1.22) and (7.1.23) for describing the nonlinear absorption. Both effects belong to the third-order nonlinear optical phenomenon in the single-photon process.

7.1.3 General Theory of Two-Photon Absorption

When two light beams at different frequencies ω_1 and ω_2 pass through the nonlinear medium simultaneously, if the sum of two photon energies is close to an energy difference of two energy levels of the medium, i.e., $\hbar\omega_1 + \hbar\omega_2 = E_2 - E_1$, one may find the two light beams at ω_1 and ω_2 simultaneously decay due to the absorption of the medium. Such phenomenon is called two-photon absorption (TPA) [1]. Figure 7.3 shows a schematic diagram of the two-photon resonance absorption. The feature of this effect is that there is a virtual energy level between two real energy levels.

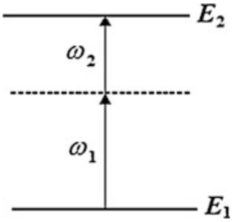


Fig. 7.3 Schematic diagram of two-photon resonance absorption

The two-photon absorption is a kind of third-order nonlinear optical effects, which can be described by a slowly-varying-amplitude-approximation nonlinear wave equation, which is

$$\frac{\partial \boldsymbol{E}(z,\omega_\mathrm{i})}{\partial z}=\frac{i\omega_\mathrm{i}}{2\varepsilon_0 cn}\boldsymbol{P}^{(3)}(z,\omega_\mathrm{i})\cdot\omega_\mathrm{i}=1,2 \tag{7.1.29}$$

Assuming there are two light waves with frequencies of ω_1 and ω_2 propagating along z direction, the field amplitudes of two lights can be written as

$$\boldsymbol{E}(z,\omega_1)=\boldsymbol{E}_0(z,\omega_1)e^{i(kz-\omega_1 t)}+c.c. \tag{7.1.30}$$

$$\boldsymbol{E}(z,\omega_2)=\boldsymbol{E}_0(z,\omega_2)e^{i(kz-\omega_2 t)}+c.c. \tag{7.1.31}$$

The nonlinear polarizations induced by these two fields are respectively

$$\boldsymbol{P}^{(3)}(\omega_1)=6\varepsilon_0\chi^{(3)}(\omega_1;\omega_2,-\omega_2,\omega_1)\boldsymbol{E}(\omega_2)\boldsymbol{E}^*(\omega_2)\boldsymbol{E}(\omega_1), \tag{7.1.32}$$

$$\boldsymbol{P}^{(3)}(\omega_2)=6\varepsilon_0\chi^{(3)}(\omega_2;\omega_1,-\omega_1,\omega_2)\boldsymbol{E}(\omega_1)\boldsymbol{E}^*(\omega_1)\boldsymbol{E}(\omega_2). \tag{7.1.33}$$

Because we only concern the absorption, taking the imaginary part of the susceptibility, and substituting Eqs. (7.1.32) and (7.1.33) into Eq. (7.1.29), then we obtain two nonlinear wave equations:

$$\frac{\partial \boldsymbol{E}(z,\omega_1)}{\partial z}=-\frac{3\omega_1}{cn_1}\chi^{(3)\prime\prime}(\omega_1;\omega_2,-\omega_2,\omega_1)\boldsymbol{E}(\omega_2)\boldsymbol{E}^*(\omega_2)\boldsymbol{E}(\omega_1), \tag{7.1.34}$$

$$\frac{\partial \boldsymbol{E}(z,\omega_2)}{\partial z}=-\frac{3\omega_2}{cn_2}\chi^{(3)\prime\prime}(\omega_2;\omega_1,-\omega_1,\omega_2)\boldsymbol{E}(\omega_1)\boldsymbol{E}^*(\omega_1)\boldsymbol{E}(\omega_2). \tag{7.1.35}$$

According to the symmetric rule of susceptibility, we have

$$\chi^{(3)\prime\prime}(\omega_1;\omega_2,-\omega_2,\omega_1)=\chi^{(3)\prime\prime}(\omega_2;\omega_1,-\omega_1,\omega_2). \tag{7.1.36}$$

Taking the procedure of Eq. (7.1.34) × $\boldsymbol{E}^*(\omega_1)$- Eq. (7.1.35) × $\boldsymbol{E}^*(\omega_2)$, we then get the following equation:

$$\frac{n_1}{\omega_1}\boldsymbol{E}^*(z,\omega_1)\frac{\partial \boldsymbol{E}(z,\omega_1)}{\partial z}-\frac{n_2}{\omega_2}\boldsymbol{E}^*(z,\omega_2)\frac{\partial \boldsymbol{E}(z,\omega_2)}{\partial z}=0. \tag{7.1.37}$$

To integrate of z on both side of Eq. (7.1.33), we obtain

$$\frac{n_1}{\omega_1}|\boldsymbol{E}(z,\omega_1)|^2-\frac{n_2}{\omega_2}|\boldsymbol{E}(z,\omega_2)|^2=\text{constant}. \tag{7.1.38}$$

Using $I_i = \frac{1}{2}c\varepsilon_0 n_i |E_i|^2 (i = 1, 2)$, Eq. (7.1.38) becomes:

$$\frac{I_1(z, \omega_1)}{\hbar\omega_1} - \frac{I_2(z, \omega_2)}{\hbar\omega_2} = \text{constant.} \tag{7.1.39}$$

To rewrite Eq. (7.1.39) to be the photon-umber relationship:

$$N(z, \omega_1) - N(z, \omega_2) = N(0, \omega_1) - N(0, \omega_2), \tag{7.1.40}$$

or

$$N(z, \omega_1) - N(0, \omega_1) = N(z, \omega_2) - N(0, \omega_2). \tag{7.1.41}$$

It shows that the two light beams at ω_1 and ω_2 are absorbed and amplified by the medium at the same time in TPA process.

On the both sides of Eq. (7.1.34) times $\boldsymbol{E}^*(z, \omega_1)$ and on the both sides of Eq. (7.1.35) time $\boldsymbol{E}^*(z, \omega_2)$, respectively, therefore TPA process can be expressed by the following two coupled equations:

$$\frac{dI_1}{dz} = -\beta_1 I_1 I_2, \tag{7.1.42}$$

$$\frac{dI_2}{dz} = -\beta_2 I_1 I_2. \tag{7.1.43}$$

where β_1 and β_2 are two-photon absorption coefficients:

$$\beta_1 = \frac{6\omega_1}{\varepsilon_0 c^2 n_1 n_2} \chi^{(3)\prime\prime}, \tag{7.1.44}$$

$$\beta_2 = \frac{6\omega_2}{\varepsilon_0 c^2 n_1 n_2} \chi^{(3)\prime\prime}. \tag{7.1.45}$$

We can see that β_1 and β_2 are all proportional to the imaginary part of the third-order nonlinear susceptibility.

Specifically, when a single light beam at the frequency ω and with the intensity I propagates in the medium, it also can generate the two-photon effect. In this case, the two photons have the same frequency: $\omega_1 = \omega_2 = \omega$. And the related two light beams have $I_1 = I_2 = I$ and $\beta_1 = \beta_2 = \beta$. TPA process in this case can be expressed by one equation, that is

$$\frac{dI}{dz} = -\beta I^2, \tag{7.1.46}$$

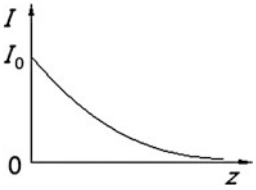


Fig. 7.4 The light intensity as a function of the propagation distant in TPA process of single light beam

where

$$\beta = \frac{6\omega}{\varepsilon_0 c^2 n^2} \chi^{(3)\prime\prime}. \tag{7.1.47}$$

If the intensity of light incident into the medium at $z = 0$ is $I(0) = I_0$, the solution of Eq. (7.1.46) will be

$$I(Z) = \frac{I_0}{1 + I_0 \beta z}. \tag{7.1.48}$$

The relation of the light intensity (I) versus the propagation distant (z) in TPA process is shown in Fig. 7.4.

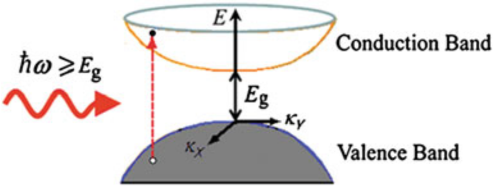
7.1.4 Two-Photon Absorption and Refraction in Semiconductor

1. **Two-Photon Absorption and Free-Carrier Absorption in Semiconductor**

In the semiconductor, there are a conduction band and a valence band, these two-band structure is equivalent to a two energy-level system. The interval between the two bands is called the forbidden band (or the bandgap). When a light beam irradiates a semiconductor medium, the light absorption phenomenon is generated: the semiconductor absorbs a photon with energy near or exceed the bandgap, i.e., $\hbar\omega \geq E_g$, it will stimulate an electron from the valence band jumping to the conduction band to be a free electron. At the same time, a hole at valence band also becomes a free hole. Both of two free-carriers bind together to form a free electron-hole pair, as shown in Fig. 7.5.

A large number of photons stimulate the electrons to generate a quantity of free electron-hole pairs, and induces the change of the free-carrier concentration, therefore it results in the change of the absorption coefficient of semiconductor. That is the nonlinear absorption phenomenon of semiconductor in the single-photon case.

Fig. 7.5 Schematic diagram of light absorption in semiconductor



The experiment also shows that if the light frequency is ω', the photon energy equals to a half of the bandgap, i.e., $\hbar\omega' = E_g/2$, it also finds the light absorption: absorbing two photons at frequency ω' to stimulate two electron-hole pairs at the same time, then change the free-carrier concentration and the absorption coefficient. That is two-photon absorption phenomenon.

A laser beam propagates in the semiconductor along the z direction, as we presented in Sect. 1.7.1, the light-intensity transmission equation is

$$\frac{dI}{dz} = -\alpha I - \beta I^2. \tag{7.1.49}$$

where α is the single-photon absorption coefficient (here $\alpha \approx \alpha_0$); β is the two-photon absorption coefficient. How can we measure the α and β by using the experimental method?

We can solve the Eq. (7.1.49) to get the following formula [2]

$$I(z) = \frac{I(0)\alpha e^{-\alpha z}}{\alpha + \beta I(0)(1 - e^{-\alpha z})}. \tag{7.1.50}$$

Taking $z = L$, Eq. (7.1.50) can be written to

$$\frac{1}{I(L)} = \frac{1}{e^{-\alpha L} I(0)} + \frac{\beta(1 - e^{-\alpha L})}{\alpha e^{-\alpha L}}, \tag{7.1.51}$$

where $I(0)$ is the input light-intensity; $I(L)$ is the output-light intensity. and L is the length of material.

Setting $Y = 1/I(L), X = 1/I(0)$, and $B = \beta(1 - e^{-\alpha L})/\alpha e^{-\alpha L}$, Eq. (7.1.51) becomes

$$Y = e^{\alpha L} X + B. \tag{7.1.52}$$

The common method of measuring nonlinear absorption coefficients is using the measured semiconductor material to make a slab waveguide with the length of L, inputting a short-pulse laser and continuously changing its power, then measuring the input intensity $I(0)$ and the output intensity $I(L)$, and taking their reciprocal values to record on a coordinate graphs of $Y - X = 1/I(L) - 1/I(0)$ as the experimental points. To connect the experimental points in a nearly straight line, as shown in Fig. 7.6. From the slope of the straight line $e^{\alpha L}$, we can calculate to obtain

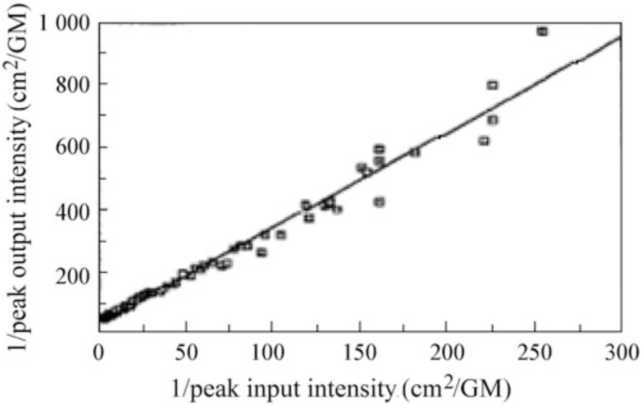


Fig. 7.6 The reciprocal input intensity as a function of the reciprocal output intensity. The experimental points obtained from an measurement form a straight line

the absorption coefficient α, and then from the intercept of the straight line on the vertical axis Y, i.e., $B = \beta(1 - e^{-\alpha L})/\alpha e^{-\alpha L}$, finally to find the value of β.

For example, a $GaAs/AlGaAs$ MQW ridge waveguide with a dimension of long × high × wide = 1 cm × 0.8 μm × 1.5–5.5 μm, using a mold-lock YAG laser at the wavelength of 1.064μm and with the pulsewidth of 90 ps as the input laser, continuously changing the input intensity, to get an experimental curve (see Fig. 7.6). The measured results are: $\alpha = 112\text{m}^{-1}$ and $\beta = 2.0 \times 10^{-10}\text{m/W}$ for TM polarization mode; $\alpha = 90\text{m}^{-1}$ and $\beta = 2.7 \times 10^{-10}\text{m/W}$ for TM polarization mode.

It is worth noting that the light source used in the experiment is a pulsed laser, the measured intensity by photodetector is the average intensity. However, the calculated intensity by the theoretical formula is the peak intensity. How to transfer the average intensity to the peak power?

We assume that the incident laser is a Gaussian beam; its intensity is a Gaussian-type time function:

$$I(t) = I_0 \exp\left(\frac{-2t^2}{T^2}\right), \tag{7.1.53}$$

where I_0 is the peak intensity, T is the full width at half maximum amplitude (FWHM). Because we define the full width at $1/e$ of maximum intensity as $\sqrt{2}T$, the phase factor of Gaussian beam is written as $\exp(-2t^2/T^2)$, as shown in Fig. 7.7.

The Fig. 7.7 shows that the time original point is located at the maximum intensity, when $t = 0$, the phase factor is $e^0 = 1$, so $I(t) = I_0$; when $t = (\sqrt{2}/2)T = T/\sqrt{2}$, the phase factor is e^{-1}, so $I(t) = (1/e)I_0$. For the Gaussian pulse, the relationship between the peak intensity I_0 and the average intensity I_{avg} can be calculated to obtain:

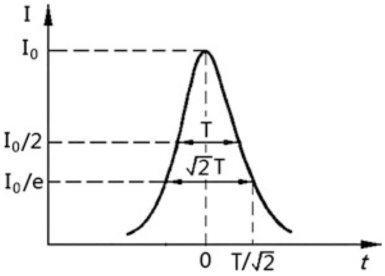


Fig. 7.7 Diagram for explaining the phase factor of Gaussian beam

$$\frac{I}{I_{avg}} = \frac{\sqrt{2t_p}}{\sqrt{\pi T}}, \tag{7.1.54}$$

where T is FWHM of the Gaussian pulse; t_p is the width of average intensity, which is the width of a square pulse, who's total energy equals to that of the Gaussian pulse. For example, in the above experiment, we used a YAG pulsed laser, the measured data are $T = 75\,ps$ and $t_p = 13\,ns$, so the ratio of the peak intensity and the average intensity is 138.

Now we substitute the measured data $\alpha = 100\,\text{m}^{-1}$, $\beta = 2 \times 10^{-10}\,\text{m/W}$, $t_p = 13\,\text{ns}$, $T = 75\,\text{ps}$ and $L = 0.01\,\text{m}$ into Eq. (7.1.51), calculating to obtain the input-output intensity curve for two-photon absorption, i.e., the $I(L) - I(0)$ curve (1), as shown in Fig. 7.8. Obviously, with the increase of the input light intensity, the output light intensity has a saturation characteristic.

In fact, in the semiconductor, there is another nonlinear absorption mechanism—free carrier absorption (FCA). The FCA mainly derives from two-photon absorption (TPA): the medium absorbs two photon energy ($2\hbar\omega$), then stimulates the electronic transition to generate the electron-hole pairs, i.e., free carriers. When measuring the two-photon absorption coefficient β by using Eq. (7.1.51), people often cannot distinguish FCA from TPA. The curve (1) shown in Fig. 7.8 includes both effects.

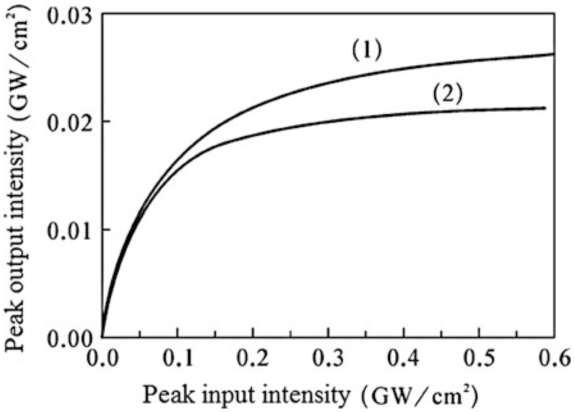


Fig. 7.8 The curve of output intensity versus input intensity for two-photon absorption obtained from the calculation. (1) without considering the effect of FCE to TPA, calculated by using Eq. (7.1.51); (2) considering the effect of FCE to TPA, calculated by using Eqs. (7.1.60) and (7.1.61)

In order to exclude FCA from the TPA measured data, we need modify Eq. (7.1.49), namely adding a new item in its right side for describing FCA [2]:

$$\frac{dI}{dz} = -\alpha I - \beta I^2 - \sigma_{\mathrm{ex}} \Delta N I. \tag{7.1.55}$$

where σ_{ex} is the total absorption cross section of free carriers; ΔN is the change of free-carrier number density, which comes from the two-photon absorption. Using Eq. (7.1.4), we have

$$\frac{dI}{dz} = \frac{d\boldsymbol{\varepsilon}}{dt} = \frac{dN}{dt}(2\,h\nu) = \beta I^2, \tag{7.1.56}$$

where $\boldsymbol{\varepsilon}$ is the light-energy density; $h\nu$ is the single-photon energy, N is the free-carrier number density and β is the two-photon absorption coefficient. Thus the change of the free-carrier umber density with the time is

$$\frac{dN}{dt} = \frac{\beta I^2}{2h\nu}. \tag{7.1.57}$$

Assuming the incident light is a Gaussian-type pulse as shown in Eq. (7.1.53), the change of the free-carrier number density under a single pulse ΔN_{P} can be found from the following integral calculation:

$$\Delta N_{\mathrm{P}} = \frac{\beta}{2h\nu} \int\limits_{-\infty}^{\infty} I_0^2 \exp\left(\frac{-4t^2}{T^2}\right) dt = \frac{\sqrt{\pi}\beta T I_0^2}{4h\nu}, \tag{7.1.58}$$

where T is FWHM of light; I_0 is the peak intensity of the light.

Actually no carrier is produced by one light pulse. If the recombination time of the carrier is τ, before this time the other pulses also have contribution to the production of the carrier. Suppose the pulse duration of the laser pulse is t_{p}, thus the change of total free-carrier number density is

$$\begin{aligned} \Delta N &= \Delta N_{\mathrm{P}} \left[1 + \exp\left(\frac{-t_{\mathrm{p}}}{\tau}\right) + \exp\left(\frac{-2t_{\mathrm{p}}}{\tau}\right) + \exp\left(\frac{-3t_{\mathrm{p}}}{\tau}\right) + \cdots \right] \\ &= \frac{\Delta N_{\mathrm{P}}}{\left[1 - \exp(-t_{\mathrm{p}}/\tau)\right]}. \end{aligned} \tag{7.1.59}$$

Substituting Eq. (7.1.59) into Eq. (7.1.55), and giving a definition of the free-carrier absorption coefficient γ, which is a physical quantity independent from the intensity:

$$\gamma = \frac{\sigma_{ex}\Delta N}{I_0^2} = \frac{\sqrt{\pi}\sigma_{ex}\beta T}{4h\nu[1 - \exp(-t_{\mathrm{P}}/\tau)]}, \tag{7.1.60}$$

and setting $\mathrm{I}_0^2 = I^2$, we then obtain

$$\frac{dI}{dz} = -\alpha I - \beta I^2 - \gamma I^3. \tag{7.1.61}$$

This is the light-intensity transmission equation including the free-carrier absorption for semiconductors.

Therefore, the total absorption coefficient of semiconductor is

$$\alpha_T = \alpha + \beta I + \gamma I^2. \tag{7.1.62}$$

The Eq. (7.1.61) can find its analytical solutions [2].

Taking the following data measured in experiments: $\alpha = 100\,\mathrm{m}^{-1}, \beta = 2 \times 10^{-10}\,\mathrm{m/W}$, $t_p = 13\,\mathrm{ns}$, $T = 75\,\mathrm{ps}$, $\tau = 30\,\mathrm{ns}$, $L = 00.01\,\mathrm{m}$, $h\nu = 1.167\,\mathrm{eV}$, and $\sigma_{ex} = 5 \times 10^{-22}\,\mathrm{m}^2$, we calculated by Eq. (7.1.60) to get $\gamma = 5.1 \times 10^{-23} m^3/W^2$, and further calculated using Eq. (7.1.61) to obtain the output-input characteristic curve, as shown in the curve (2) of Fig. 7.8.

When eliminating the action of FCE, we can see that the TPA output-input curve (2) has stronger saturation feature compared with the curve (1), and the value of β becomes smaller. The calculation showed that the value of β reduced from $2.0 \times 10^{-10}\,\mathrm{m/W}$ to $1.5 \times 10^{-10}\,\mathrm{m/W}$ for TM polarization mode; and from $2.7 \times 10^{-10}\,\mathrm{m/W}$ to $2.0 \times 10^{-10}\,\mathrm{m/W}$ for TE polarization mode.

Therefore, it can be seen that although the influence of FCE to TPA is not very big, this effect cannot be ignored.

2. Two-Photon Absorption Induced Refractive-Index Variation in Silicon

In this section we will discuss the interaction between the femtosecond laser at the wavelength of 1.55 μm and the silicon material. The laser induces the two-photon absorption effect, and produces the refractive-index variation of material. In the TPA process, the two photons are absorbed by the semiconductor material to produce two electron-hole pairs. The absorption of two photons at the same time causes the free electron-density change ΔN_e and the free hole-density change ΔN_h in the semiconductor. The change of the carrier density can induce the refractive-index variation Δn and the absorption-coefficient variation $\Delta\alpha$ of the semiconductor. The calculation according to the Drude model obtains the following two equations [3]:

$$\Delta n = -\frac{e^2\lambda^2}{8\pi^2 c^2 \varepsilon_0 n}\left(\frac{\Delta N_e}{m_{ce}^*} + \frac{\Delta N_h}{m_{ch}^*}\right), \tag{7.1.63}$$

$$\Delta\alpha = \frac{e^2\lambda^3}{4\pi^2 c^3 \varepsilon_0 n}\left(\frac{\Delta N_e}{\mu_e\left(m_{ce}^*\right)^2} + \frac{\Delta N_h}{\mu_h\left(m_{ch}^*\right)^2}\right), \tag{7.1.64}$$

where e is electron charge, ε_0 is dielectric constant in free space; n is linear refractive index of material; c is light velocity; m_0 is electron mass; m_{ce}^* is electron conductivity effective mass, $m_{ce}^* = 0.26m_0$; m_{ch}^* is hole conductivity effective mass, $m_{ch}^* = 0.39m_0$; μ_e is electron mobility; μ_h is hole mobility; ΔN_e is electron-number change in every cube centimeter; ΔN_h is hole-number change in every cube centimeter.

According to the absorption spectrum obtained from experiments and calculation using the K–K relation, the relationship between the refractive-index change and the carrier-number-density change at the wavelength of 1.55 μm in silicon can be obtained [3]:

$$\Delta n = \Delta n_e + \Delta n_h = -\left[8.8 \times 10^{-22}\Delta N_e + 8.5 \times 10^{-22}(\Delta N_h)^{0.8}\right], \tag{7.1.65}$$

where Δn_e represents the refractive-index change induced by electron-number-density change ΔN_e; Δn_h represents the refractive-index change induced by hole-number-density change ΔN_h. The minus symbol in Eq. (7.1.65) shows that the increase of the free-carrier density results in the decrease of the refractive index of material.

Assuming the electron-number-density change equals to the hole-number-density change, i.e., $\Delta N_e = \Delta N_h = \Delta N$, and the incident light is a Gaussian-type pulse, the free-carrier–number- density change due to the two-photon absorption is expressed by Eq. (7.1.58), that is

$$\Delta N = \frac{\sqrt{\pi}\beta T_0^2}{4\,hv} = \frac{\sqrt{\pi}\beta TP^2}{4\,hvS^2}. \tag{7.1.66}$$

where β is the two-photon absorption coefficient; hv is a photon energy; T is the FWHM of the Gaussian pulse; P is the peak power of the light; S is the cross section of the silicon waveguide. In addition, according to Eq. (7.1.54), the ratio between the peak power P and the average power P_{avg} is given by

$$\frac{P}{P_{avg}} = \frac{\sqrt{2}t_p}{\sqrt{\pi}T}. \tag{7.1.67}$$

Substituting Eqs. (7.1.66) and (7.1.66) into Eq. (7.1.65), we obtain the refractive-index change as a function of the average power of pump light for silicon materials, that is

$$\begin{aligned}\Delta n &= \Delta n_e + \Delta n_h \\ &= -\left[8.8 \times 10^{-22}\frac{\beta t_\mathrm{p}^2}{2\,hv\sqrt{\pi}TS^2}P_{avg}^2 + 8.5 \times 10^{-22}\left(\frac{\beta t_p^2}{2\,hv\sqrt{\pi}TS^2}P_{avg}^2\right)^{0.8}\right].\end{aligned} \tag{7.1.68}$$

It is clear that in the case of two-photon absorption under the action of a femtosecond pulse laser, the refractive-index change is approximately proportional to the square of the average power ($\Delta n \propto P_{avg}^2$). However in the case of single-photon absorption under the action of CW laser or wide-width pulsed laser (up to the picosecond) being proportional to the light peak power ($\Delta n \propto P$), i.e., the Kerr effect. That is to say, in silicon materials, the optical nonlinearity based on the TPA is much stronger than that based on the Kerr effect.

In Chap. 10 we will introduce the all-optical switches in a silicon ridge nanowaveguide microring, which is based on TPA effect. The device is bumped by a femtosecond laser. The switching power of the device is lower about 10 mW, which is reduced in 1000 time compared with the Kerr effect based all-optical switches.

However, TPA effect in silicon induces the FCA effect, which reduces the switching time of devices due to the long free-carrier recombination time ($\sim$1 ns). The switching time of the TPA based all-optical switches can only reach about 100 ps. In order to overcome the speed limitations due to the FCA effect, scientists suggest using a silicon–organic hybrid (SOH) approach, which is to replace the silicon ridge waveguide with a silicon slotted waveguide filled with a nonlinear organic molecular material. Therefore these all-optical switches have fast response time due to the Kerr effect, their switching time can be less than 10 ps.

7.2 Saturable Absorption and Reverse Saturable Absorption

Previous section discussed two kinds of nonlinear optical absorptions: the single-photon absorption and the two-photon absorption under the condition of the light-matter interaction away from resonance. We only studied the third-order nonlinear optical process. This section will discuss another two kinds of nonlinear optical absorptions: the saturable absorption and the reverse saturable absorption. Because they are under the condition of the light-matter interaction on the resonance, we should use the energy-level-transition model of molecules (or atoms) to describe. Actuary, the model implies the all different high order nonlinear optical processes.

7.2.1 Molecular-Energy-Level Model of Saturable Absorption

1. **Macroscopical Characteristics of Saturable Absorption**

Many experiments show that, when a laser irradiates some organic materials, the absorption coefficient of the material will decrease with the increase of light intensity, until reaching a saturation value. This effect is known as the saturable absorption (RS). The relationship between the absorption coefficient $\alpha(I)$ and the light intensity I is expressed as [4]

$$\alpha(I) = \frac{\alpha_0}{1 + \frac{I}{I_c}}. \tag{7.2.1}$$

where α_0 is the linear absorption coefficient of the material; I_c is the saturation intensity, which depends on the property of material.

Figure 7.9 shows a curve of the absorption coefficient as a function of the light intensity. In the figure, the vertical axis denotes the absorption coefficient of $\alpha(I)$; the horizontal axis denotes the relative light intensity of I/I_c, here I_c is the saturation intensity, which determines the speed of absorption saturation with the increase of the light intensity. We can see that if I_c is smaller, the $\alpha(I)$ declines faster; when $I \approx 0, \alpha = \alpha_0$; when $I = I_c, \alpha = \alpha_0/2$; and when $I \to \infty, \alpha \to 0$.

Assuming the length of the medium is L, the incident light intensity is $I(0)$, and the transmitted light intensity is $I(L)$, in the case of the saturable absorption, the transmission of medium is

$$T = \frac{I(L)}{I(0)} = e^{-\alpha(I)L}. \tag{7.2.2}$$

According to Eqs. (7.2.2) and (7.2.1), the transmission of medium increase with the increase of the intensity until to $T = 1$ when $I \to \infty$. It means that the medium becomes transparent under a strong light intensity, this phenomenon is called as "bleaching".

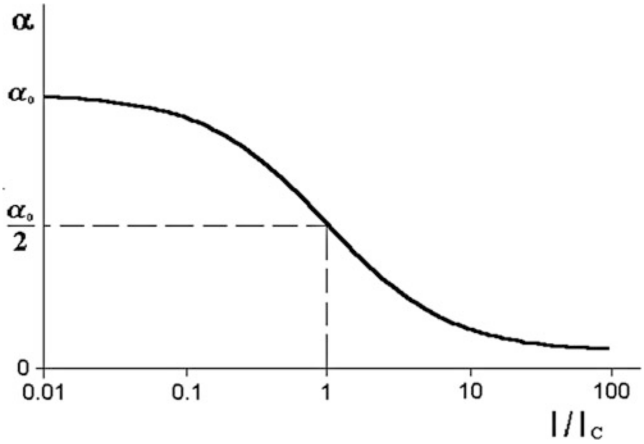


Fig. 7.9 Characteristic curve of the saturable absorption

In the 1970s the saturable absorption is widely applied in the laser-pulse compression techniques, such as Q-switching and mode locking [5]. In the 1980s, scientists studied the intrinsic optical bistable devices, which are based on the saturable absorption effect [6].

The saturable absorption cannot be described by the nonlinear polarization theory, but it can be simply explained by the energy-level transition model of microcosmic particle (molecule, ion or atom) system under the laser's action. When the particles in the ground state absorb the energy of photons of extraneous laser and jump to the first excited states, if the laser is strong enough, it will make the absorption of system to be saturation. This is the origin of the saturable absorption phenomenon. Here we are going to discuss the two-level and three-level model for the saturable absorption by using the rate equation theory [7].

2. Two Energy-Level Model of Saturable Absorption

Firstly we consider the saturable absorption in a simple two-level molecular model, which consists of the ground-state S_0 with energy ε_1 and molecular-number density n_1 and the first excited-state S_1 with energy ε_2 and molecular-number density n_2, as shown in Fig. 7.10.

Under the resonance interaction between the light at frequency ω, with intensity I and the two-level molecular medium, the photon energy equals to the difference of two-level energies, i.e., $\hbar\omega = \varepsilon_1 - \varepsilon_0$. The molecules on the ground-state absorb the photons jumping to the excited state as a stimulated transition with an absorption cross section (or a transition probability) of σ_0. Because the lifetime of molecule in the excited-state is very short, the molecules return to the ground-state from the excited-state through two ways: the most of molecules through the spontaneous radiation (or non-radiation) with a relaxation time τ_{21} (or a transition probability $1/\tau_{21}$); only a part of molecules come back to ground-state through the stimulated radiation with the same transition probability of σ_0.

Denoting the total molecule-number density as N, the change of n_2 with the time is described by the following rate equations:

$$\frac{\partial n_2}{\partial t} = \frac{\sigma_0}{\hbar\omega} I(n_1 - n_2) - \frac{n_2}{\tau_{21}}, \tag{7.2.3}$$

and

$$N = n_1 + n_2. \tag{7.2.4}$$

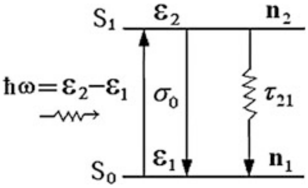


Fig. 7.10 Light-induced saturable absorption in a two-level molecular model

When the pulsewidth of laser is much larger than the molecule relaxation time, i.e., $\tau_L > > \tau_{21}$, it can be treated as meeting the steady-state condition, so $\partial/\partial t = 0$ in Eq. (7.2.3), then we obtain the difference of molecule-number density between the two energy levels, that is

$$\Delta n = n_1 - n_2 = \frac{N}{1 + \frac{I}{I_c}}, \tag{7.2.5}$$

where I_c is the saturation intensity defined as

$$I_c = \frac{\hbar\omega}{2\sigma_0\tau_{21}}. \tag{7.2.6}$$

When $I = 0$, the linear absorption coefficient is

$$\alpha_0 = N\sigma_0, \tag{7.2.7}$$

When $I \neq 0$, the nonlinear absorption coefficient is

$$\alpha(I) = \Delta n(I)\sigma_0. \tag{7.2.8}$$

Substituting Eqs. (7.2.7) and (7.2.8) into Eq. (7.2.5), then we obtain Eq. (7.2.1) for the saturable absorption:

$$\alpha(I) = \frac{\alpha_0}{1 + \frac{I}{I_c}}.$$

We can see that when $I \to \infty, \Delta n \to 0$, then $n_1 \approx n_2$. That is to say, under the action of a strong light, through the transition of molecules $S_0 \to S_1$ and $S_1 \to S_0$, the molecule-number density of the ground state equals to that of the excited state. It means that the molecular system achieves a balance state, the photons cannot be absorbed by the medium again, and the light will totally pass through the medium. This is the essence of the absorption saturation of a two-energy-level system.

The semiconductor material has two energy bands with different energy: the conduction band and the valence band. So we can regard the semiconductor as a two energy-level system. Figure 7.11 shows an experimental curve for a $GaAs/GaAlAs$ MQW material with a length of L [6]. The curve shows the exciton absorption $\alpha_{\text{ex}}L$ as a function of the light intensity I, i.e., a $\alpha_{ex}L - I$ curve. The wavelength of incident laser at 0.85μm is just at the peak of the exciton absorption spectrum.

From Fig. 7.11 we can see that when the light intensity $I \to \infty$, the exciton absorption coefficient α_{ex} does not go to zero, but tends to a value of $\alpha_{\text{ex}}L = 0.26$. It shows the existence of other absorption effects. Later we will point out that this effect mainly comes from the excited-states nonlinear absorption.

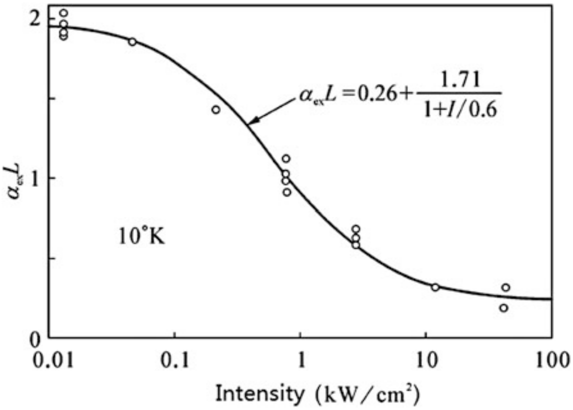


Fig. 7.11 Curve of the exciton absorption as a function of the light intensity in a *GaAs*/*GaAlAs* MQW material with a length of *L* under 10 K low temperature, the wavelength of laser is 0.85 μm

3. Three Energy-Level Model of Saturable Absorption

In dye-molecule materials, there are a singlet energy-level system and a triplet energy-level system; each of them can be regarded as a two-level system. The saturable absorption of dye molecules can be regarded as a three-level model with two excited-state level S_1, T_1 and a mutual ground-state level S_0, as shown in Fig. 7.12.

The molecules on the ground state S_0 absorb the extraneous photons, and jump to the singlet excited state S_1 with an absorption section σ_0. The molecules on the state S_1 transit to the triple excited state T_1 with a large probability of $1/\tau_{23}$. Only a small number of molecules on the state S_1 directly go back to the state S_0. Because of the probability of $1/\tau_{21}$ being very small, a large number of molecules accumulate in the state T_1. Under a strong incident light intensity, the number of molecules on the state T_1 will reach to a saturation value that equals to the total number of the molecular system.

The rate equations for describing the change of molecule number density n_1, n_3 and n_1 with the time for the three excited states S_1, T_1 and S_0 are expressed as respectively [7]

$$\frac{\partial n_2}{\partial t} = \frac{\sigma_0}{\hbar\omega} I(n_1 - n_2) - \frac{n_2}{\tau_{21}} - \frac{n_2}{\tau_{23}}, \tag{7.2.9}$$

$$\frac{\partial n_3}{\partial t} = \frac{n_2}{\tau_{23}} - \frac{n_3}{\tau_{31}}, \tag{7.2.10}$$

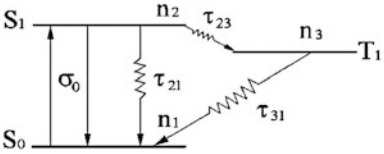


Fig. 7.12 Three-level model for explaining the saturable absorption in dye-molecule materials

$$n_1 + n_2 + n_3 = N, \tag{7.2.11}$$

where N is the total molecule number density of the system.

In the steady-state condition, we have $\partial/\partial t = 0$. Considering $\tau_{31}, \tau_{21} > > \tau_{23}$, the solutions of above three equations will be

$$n_1 = \frac{N}{1 + \frac{I}{I_c}}, \tag{7.2.12}$$

$$n_2 \approx 0, \tag{7.2.13}$$

$$n_3 = \frac{N}{1 + \frac{I_c}{I}}, \tag{7.2.14}$$

where I_c is the saturation intensity of the three-level system, which is

$$I_{\mathrm{c}} = \frac{\hbar\omega}{\sigma_0 \tau_{31}}. \tag{7.2.15}$$

The linear and nonlinear absorption coefficients are respectively

$$\alpha_0 = N\sigma_0, \tag{7.2.16}$$

$$\alpha = \Delta n \sigma_0 \cong n_1 \sigma_0. \tag{7.2.17}$$

From Eqs. (7.2.16), (7.2.17) to (7.2.12), we obtain the absorption coefficient Formula (7.2.1) again. It is obviously, the law of the saturable absorption of the three-level model is the same as that of the two-level model. However, the physical conception of absorption saturation for both models is different. From Eqs. (7.2.12) to (7.2.14) we can see, when $I \to \infty$ and $n_1 \to \infty$, then $n_3 \to N$. It means that the all of molecules transfer from the ground-state to the triplet excited-state via the singlet excited-state under a strong incident light. As a result, the system cannot absorb photons again. This is the essence of the absorption saturation for the three-level system.

The saturable absorption phenomenon mainly occurs at the peak wavelength of the linear absorption spectrum (i.e., the resonance absorption region), where the absorption coefficient has very strong intensity-dependence, i.e., the system has a strong optical nonlinearity.

7.2.2 *Relation Between Saturable Absorption and Three-Order Nonlinear Absorption*

Formerly we pointed out that the relationship between the absorption coefficient and the light intensity in the case of the third-order nonlinear polarization is linear as shown in Fig. 7.2. However, based on what we have derived from the rate equations, the relationship between those two is saturable as shown in Fig. 7.9, which is not a line relationship. How to explain this difference? Our interpretation is that the saturated absorption is a nonlinear resonant absorption based on the energy-level transition process, implicating that the saturated absorption of the system includes the contributions of each order nonlinear polarization effects, not only the third-order nonlinear polarization effect. Here we want to prove that the third-order nonlinear absorption is only a linear approximation of the saturated absorption under the weak intensity.

Now we consider a two-level system bumped by a laser beam. The saturation intensity of this system I_c is expressed by Eq. (7.2.6). When the intensity in the medium I is very small then I_c, i.e., $I < < I_c$, we take the Taylor series expansion for Eq. (7.2.1), and only keep the linear approximation item, the nonlinear absorption coefficient of the system will be

$$\alpha = \alpha_0 \left(1 + \frac{I}{I_c}\right)^{-1} \approx \alpha_0 \left(1 - \frac{I}{I_c}\right) = \alpha_0 - \frac{\alpha_0}{I_c} I. \tag{7.2.18}$$

In this case, the absorption coefficient is a linear function of the light intensity, as shown in Fig. 7.13.

In compare with Eq. (7.2.18): $\alpha = \alpha_0 - |\alpha_2| I$, we have

$$|\alpha_2| = \frac{\alpha_0}{I_c}, \tag{7.2.19}$$

In short, the third-order nonlinear absorption is a linear approximation of the saturated absorption under the condition of $I < < I_c$.

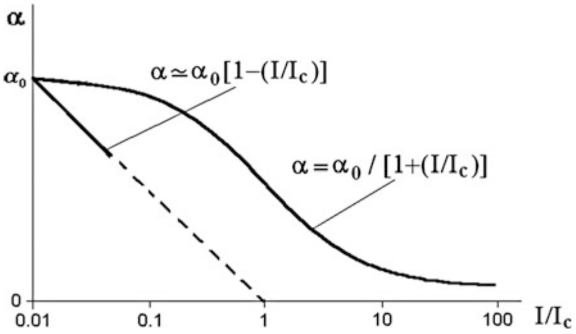


Fig. 7.13 The comparison of the saturable absorption and the third-order nonlinear absorption

7.2.3 Molecular-Energy-Level Mode of Reverse Saturable Absorption

1. **Five-Level Model of Reverse Saturable Absorption** [8]

An effect is called as the reverse saturable absorption (RSA) in which the absorption coefficient increases with the increase of the light intensity, as shown in Fig. 7.14. In the figure, α is the absorption coefficient of the medium; I is the light intensity in the medium; and α_0 is the linear absorption coefficient, i.e., low-intensity absorption coefficient of the medium.

RSA is a nonlinear optical absorption caused by the transitions between excited states under a strong light radiation. The large organic molecules have a large number of energy levels. Within the non-resonance wavelength area, the ground-state absorption is weak; but the excited-state nonlinear absorption may appear stronger, it is possible to generate the RSA.

In order to describe the reverse saturable absorption in the organic large molecules, a five-level model is used, which is consisted of the singlet and triplet two energy-level systems, as show in Fig. 7.15.

In Fig. 7.15, $0, 1, 2, 3, 4, \ldots$ denotes the lowest electronic energy-level; and $1', 2', 3', 4', \ldots$ denotes the upper vibration and rotation energy levels. S_0 is the ground-state level, S_1 and S_2 are the first and a higher excited-state levels in the singlet system. T_1 and T_2 are the first and the higher excited-state levels in the triplet system. When a laser beam at the frequency ω irradiates the molecule system, the molecules on electronic level 0,1,3 simultaneously absorb the photons at the frequency ω, and jump to the sublevels $1', 2', 4'$ with the absorption cross-section $\sigma_0, \sigma_S, \sigma_T$, respectively. Because the life time of the molecules in these sublevels is very short (shorter than a picosecond), the molecules jump down to the lower levels of 1, 2, 4 through a rapid relaxation, then down to the level 0, 1, 3 by the nonradioactive relaxation. At the room temperature, the stimulated emission of organic molecules is in a very small probability, it can be ignored. The lifetime of levels 1 and 3 are τ_S (about tens of nanoseconds) and τ_T (up to microseconds or more), respectively.

The inter-system relaxation time τ_{ST} in the transition between levels 1–3 is generally short (nanoseconds or sub-nanoseconds), namely $\tau_{ST} << \tau_{S0}$ and τ_{T0},

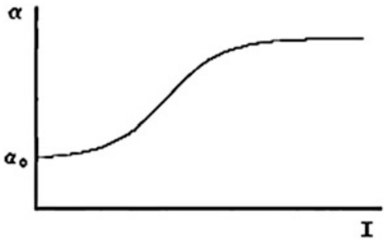


Fig. 7.14 Characteristic curve of the reverse saturable absorption

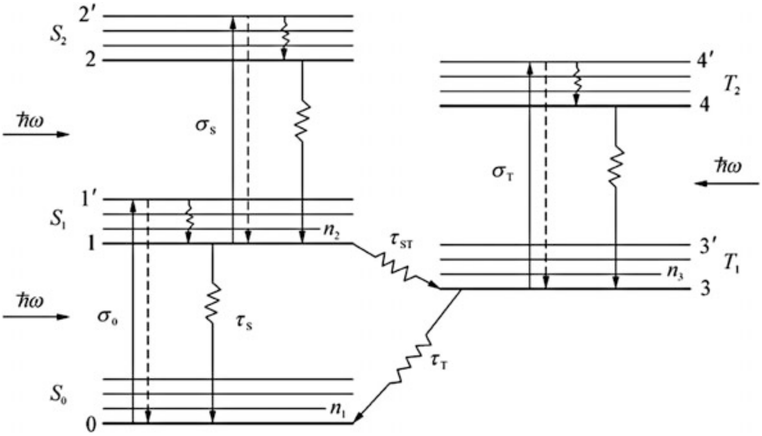


Fig. 7.15 Five-level model of organic large molecules for explaining the reverse saturable absorption

hence its transition probability is great. Because the probability from excited state T_1 to S_0 is very small, the most of molecules accumulate to the level 3.

Under the excitation of a laser, except the stimulated absorption from the electronic level 0, 1, 3 to the sublevels $1', 2', 4'$, existing also the stimulated absorption $S_1 \rightarrow S_2$ and $T_1 \rightarrow T_2$, they all contribute to the change of the total absorption coefficient. However the lifetimes of state S_2 and T_2 are very short ($\leq$ps), the probability for remaining in these states is very little, so molecule-number density in these two high energy levels can be ignored. We just consider the changes of molecule-number densities n_1, n_2 and n_3 at the energy levels S_0, S_1 and T_1 with the time.

In the large organic molecules with the central symmetry, there are a large number of energy levels and easy to generate the RSA, which is suitable to explain by using the above five-level model. For example, the metal phthalocyanine (MPc) molecules with two dimensional π-electronic mechanism and the C_{60} molecules with three dimensional π-electronic mechanism as shown in Fig. 7.16a, b respectively. There are many vibration and rotation levels near every electronic level, it makes a possibility that the molecules in ground-state and the excited-state of single or triple energy-level systems absorbing the photons with the same frequency at the same time. Figure 7.16c, d illustrates the linear absorption spectrum of MPc and C_{60}. It is visible that near the peak of linear absorption spectrum (in resonance region), the ground-state absorption is much greater than the excited-state absorption, i.e., $\sigma_0 > > \sigma_S$ and σ_T, the saturable absorption occurs only. However, near the wavelength of 500 nm at the valley of the ground-state absorption spectrum (in unresonance area), the excited-state absorption might be greater than the ground-state absorption, i.e., $\sigma_S > \sigma_0$ and $\sigma_T > \sigma_0$, so the reverse saturable absorption can be realized.

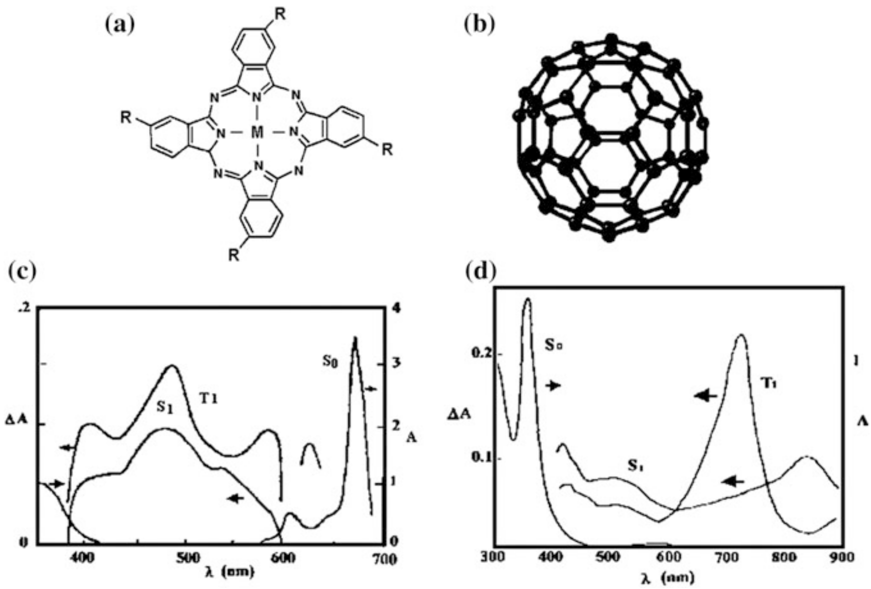


Fig. 7.16 The π-electron organic molecular structures: **a** MP_C; **b**C_{60}. The ground-state and the excited-state absorption spectra: **c** MP_C; **d**C_{60}

2. **Dynamic Equation Solution of Reverse Saturable Absorption** [9, 10]

In order to find the relationship between the absorption coefficient and the light intensity for RSA, we need build three rate-equations for molecule-number densities of n_1, n_2 and n_3, in addition, we also should build a light-intensity propagation equation. So the following four dynamic equations are established for solving the four unknowns: the molecule number densities $n_1(t), n_2(t), n_3(t)$ and the intensity $I(z,t)$:

$$\frac{\partial n_2}{\partial t} = \frac{\sigma_0 I n_1}{\hbar\omega} - \frac{n_2}{\tau_{S0}} - \frac{n_2}{\tau_{ST}}, \tag{7.2.20}$$

$$\frac{\partial n_3}{\partial t} = \frac{n_2}{\tau_{ST}} - \frac{n_3}{\tau_{T0}}, \tag{7.2.21}$$

$$n_1 + n_2 + n_3 = N, \tag{7.2.22}$$

$$\frac{\partial I(z,t)}{\partial z} = -\alpha(I) I(z,t), \tag{7.2.23}$$

where

$$\alpha(I) = \sigma_0 n_1 + \sigma_S n_2 + \sigma_T n_3. \tag{7.2.24}$$

In Eq. (7.2.24), the $\sigma_0 n_1, \sigma_S n_2$ and $\sigma_T n_3$ are the contributors of levels S_0, S_1 and T_1 to the total absorption coefficient of the system respectively. In general, in a molecular system, if the interaction among the molecules is relatively weak, the total absorption coefficient α equals to the sum of the every energy-level absorption coefficient $\alpha_i (i = 1, 2, 3, \ldots)$, and α_i is a product of the molecule-number density n_i and the absorption cross-section σ_i of the every electron energy level. If the molecular medium has m electron energy levels, the total absorption coefficient α is

$$\alpha = \sum_{i=1}^{m} \alpha_i = \sum_{i=1}^{m} \sigma_i n_i \cdot i = 1, 2, 3, \ldots, m \tag{7.2.25}$$

If the incident laser is assumed a Gaussian-type light pulse, its intensity at the position z and time t can be written as (see (7.1.53))

$$I(z,t) = I(z) e^{-2(t/\tau_L)^2}, \tag{7.2.26}$$

where $I(z)$ is the intensity at $t = 0$, τ_L is the full width at half maximum amplitude (FWHM) of the laser pulse. Actually, in the experiments with a pulsed laser source, the quantity measured by the photodetector is not the intensity $I(z,t)$, but the fluence $F(z)$, which is defined as

$$F(z) = \int_{-\infty}^{\infty} I(z,t) dt. \tag{7.2.27}$$

The dynamic Eqs. (7.2.20)–(7.2.24) and Eqs. (7.2.26) and (7.2.27) have the time and space variables. We should numerically solve these equations by using computer.

If we know the incident fluence $F(0)$ and the thickness of sample L, we can calculate to get the output fluence $F(L)$ and the transmittace $T = F(L)/F(0)$ as a function of $F(0)$, i.e., T–$F(0)$ cueve. Because $T = e^{-\alpha L}$, in terms of RSA, the absorption coefficient increases with the increase of the light intensity, it means that the transmittance will decrease with the increase of the light intensity.

We have done a experiment to prove above theoretical results. In the experiment, the RSA sample is a C_{60}-toluene solution with concentration of 7.2×10^{-4}M filled in a liquid cell with thickness of 5 mm. The RSA characteristic is described by a five-level model. The absorption cross sections of the C_{60}-toluene solution are $\sigma_0 = 2.87 \times 10^{-18}\text{cm}^2$, $\sigma_S = 1.57 \times 10^{-17}\text{cm}^2$ and $\sigma_T = 9.22 \times 10^{-18}\text{cm}^2$. The relaxation times are $\tau_{S0} = 30$ ns, $\tau_{T0} = 280$ μs and $\tau_{ST} = 1.2$ ns. The light source is a frequency-doubled YAG laser at wavelength of 532 nm. This laser can output respectively two kinds of light pulses with pulsewidth of 8 ns and 21 ps.

Under these two incident laser pulses, we obtained two experiment curves of T–$F(0)$ for RSA which is consistent with our theoretical calculation results in the range of $F(0) = 1 - 10^3\ \text{mJ}/\text{cm}^2$, as shown in Fig. 7.17.

We can see that the RSA effect in ps-pulse case is stronger than that in ns-pulse case. When the incident fluence is larger than 1 J/cm^2, the theoretical curve in ns

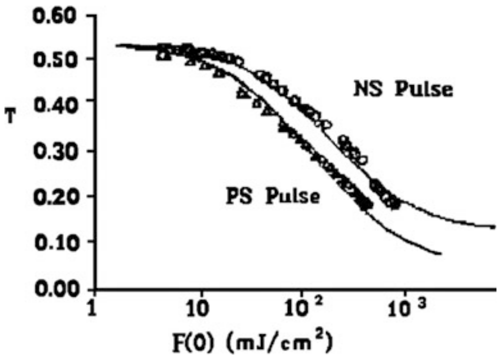


Fig. 7.17 Theoretical and experimental curves of the energy transmittance T versus the incident fluence $F(0)$ for the C_{60}-toluene solution under two lasers with pulsewidth of 8 ns and 21 ps

case is different from the experimental curve due to the other effects, such as thermal effect, diffraction, two-photon absorption, and light-induced material damage and so on.

RSA theory based on five-level molecular model shows that when the laser pulsewidth τ_L is greater than the singlet-triplet relaxation time, i.e., $\tau_L > \tau_{ST}$, for instance, the ns-light pulse inputs the molecular system with the inter-system relaxation time of ≤1 ns. In this case the molecules instantly pass through the singlet excited state to the triplet excited state, then the triplet excited-state absorption ($\alpha_3 = \sigma_T n_3$) plays a dominant role. The condition to realize RSA is $\sigma_T > \sigma_0$. Therefore, when incident light pulse with nanosecond pulsewidth, the five-level model can be simplified to be the three-level model (S_0-T_1-T_2), as shown in Fig. 7.18a.

However, when the laser pulsewidth is small than the singlet-triplet relaxation time, i.e., $\tau_L < \tau_{ST}$, for instance, the ps-light pulse inputs the molecular system with the inter-system relaxation time of ≤1 ns. In this case the molecules cannot transit to the triplet system from the singlet system, then the singlet excited-state absorption ($\alpha_2 = \sigma_S n_2$) plays a dominant role. In this case the condition to realize RSA is $\sigma_S > \sigma_0$. So the five-level model can be simplified to be the three-level model (S_0-S_1-S_2), as shown in Fig. 7.18b.

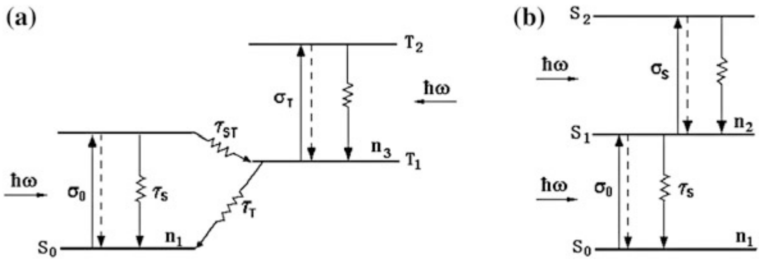


Fig. 7.18 Simplified RSA molecular models: **a** the three-level model (S_0-T_1-T_2) when inputting a ns light pulse: **b** the three-level model (S_0-S_1-S_2) when inputting the ps light pulse

3. **Steady-State Equation Solutions** [10]

When the pulsewidth of incident light pulse τ_L is much larger than the life times of all excited energy-levels, the nonlinear optical absorption process can deal with as a steady-state problem, namely $\partial/\partial t = 0$ in Eqs. (2.2.20) and (2.2.21). Assuming $\tau_{\mathrm{T0}} > > \tau_{\mathrm{ST}}$ and $\tau_{\mathrm{S0}} > > \tau_{\mathrm{ST}}$, the solutions of rate equations for n_1, n_2 and n_3 are

$$n_1 = \frac{N}{1 + \frac{I}{I_c}}, \tag{7.2.28}$$

$$n_2 \approx 0, \tag{7.2.29}$$

$$n_3 = \frac{N}{1 + \frac{I_c}{I}}, \tag{7.2.30}$$

where

$$I_c = \frac{\hbar\omega}{\sigma_0 \tau_{\mathrm{TO}}}. \tag{7.2.31}$$

Considering

$$\alpha_0 = N\sigma_0, \tag{7.2.32}$$

$$\alpha = n_1\sigma_0 + n_3\sigma_T, \tag{7.2.33}$$

We obtain

$$\alpha = \alpha_0 \left[\frac{1 + \left(\frac{\sigma_T}{\sigma_0}\right)\frac{I}{I_c}}{1 + \frac{I}{I_c}} \right]. \tag{7.2.34}$$

The curves of the absorption coefficient α as a function of the intensity I for different $\sigma_{\mathrm{T}}/\sigma_0$ is shown in Fig. 7.19, in which the saturation intensity is $I_{\mathrm{c}} = 10^5$ W/cm^2. From the figure we can see when $\sigma_T < \sigma_0$ the curves belong to the saturable absorption; when $\sigma_T > \sigma_0$, the curves belong to the reveres saturable absorption; when $\sigma_T = \sigma_0, \alpha = \alpha_0$, the curve is a straight line; when $I \to \infty, \alpha \to \alpha_0(\sigma_T/\sigma_0)$; when $I = I_c$, $\alpha = (\alpha_0/2)[1 + (\sigma_{\mathrm{T}}/\sigma_0)]$.

In addition using the rate-equation theory to study the RSA in five-energy-level molecular system; we also used the density matrix theory to study the RSA in multiple energy-level system [11]. We have found the conversion effects between RSA and SA [12, 13], as well as the conditions of the conversion between RSA and SA [14].

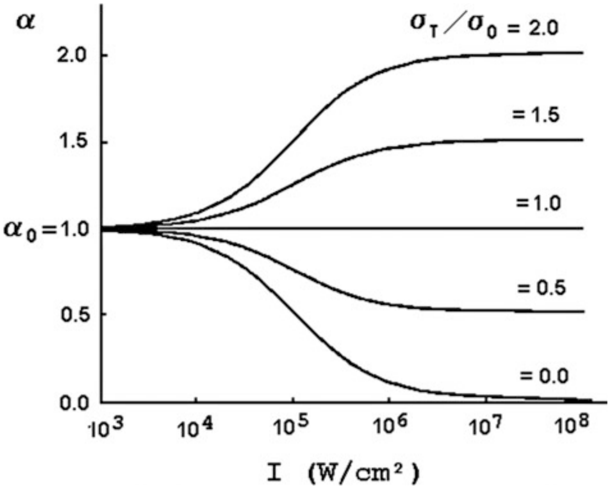


Fig. 7.19 Relationship between the absorption coefficient α and the intensity I under the different σ_T/σ_0 and $I_c = 10^5$ W/cm^2

7.2.4 Application of Reverse Saturable Absorption in All-Optical Limiting

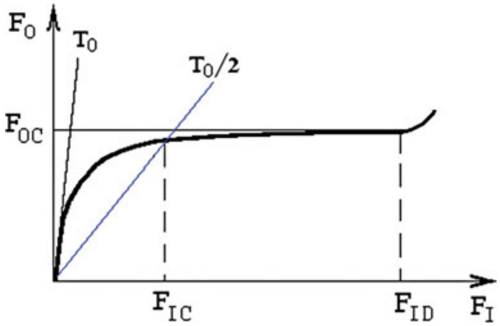
Researches on the nonlinear optical absorption and related various excited-state nonlinear effects deepen the people's understanding to the interaction between light and matter. On this basis, it opens up a new field of an excited-state nonlinear optics.

Revers saturated absorption can be used as an kind of all-optical bistable devices, which is the enhanced-absorption-type mirrorless devices [6]. Another important application of RSA is for laser protection, made into a nonlinear optical limiters to protect the human eyes or photodetectors from laser weapon damage [15–18].

A characteristic curve of nonlinear optical limiters is shown in Fig. 7.20. In the figure, F_I is the incident fluence, F_0 is the outputted fluence, F_{IC} is the limiting threshold of incident fluence, F_{0C} is the limiting threshold of outputted fluence, F_{ID} is damage threshold of incident fluence, $F_{ID} - F_{IC}$ is the dynamic range for incident fluence, T_0 is the linear transmittance.

As an example of the nonlinear optical limiter, Fig. 7.21 shows the working principle of a grating-type optical limiter under a strong laser pulse. This nonlinear optical limiter is made up of two pieces of quartz gratings sandwiched with a nonlinear organic liquid film. The refractive index of the organic liquid is matched with the quartz (about $n_0 = 1.5$) in ordinary case without laser pulse, and then the incident light can pass through the device with a high transmittance. However, under a strong laser pulse to make the liquid vaporization, the refractive index of liquid will be changed about $\Delta n \approx 0.5$, and then the laser beam will be scattered by the gratings.

Fig. 7.20 A characteristic curve of nonlinear optical limiters



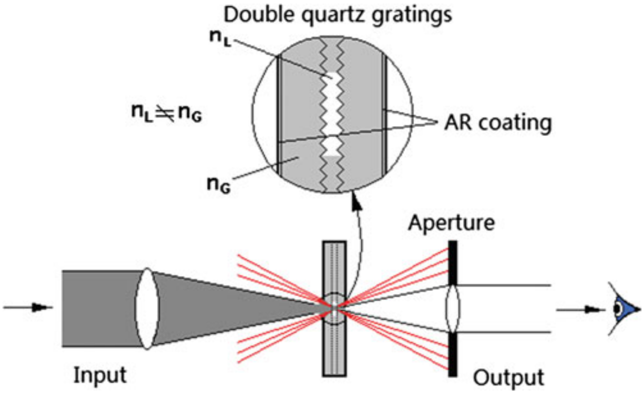


Fig. 7.21 Schematic diagram of a grating-type nonlinear optical limiter

Because of the grating is designed to be that the zero-order scattering intensity is zero, so the incident light is blocked by a small aperture in front of the eyes of observer, thus the optical limiter can protect human eyes from the laser damage.

The device performance parameters are: the linear transmittance >80 %; the output limiting threshold <0.5 mJ/cm^2 (just small than the eye-damage threshold); the dynamic range of $F_{ID} - F_{IC} > 10^4$; the response time of ns, the spectral range of 400–700 nm.

7.3 Saturable Refraction and Reverse Saturable Refraction

7.3.1 Description of Saturable Refraction and Reverse Saturable Refraction [19, 20]

We have mentioned before in the last section, if the interaction among molecules is weak, and the molecular system has *m* energy-levels, the system's absorption coefficient α equals to the sum of the absorption coefficients contributed by individual energy level α_i, the α_i is proportional to the molecular-number density of the corresponding energy level N_i, the ratio is just the absorption cross-section σ_i as described by Eq. (7.2.25).

When the light irradiates a molecular system to make the energy-level transition of molecules, resulting in the absorption-coefficient change, according to K-K relation, the refractivity-index of system is also to be changed. We can regard that the total refractivity-index of molecular system n equals to the sum of the every energy-level contributed refractivity index n_i, but it should plus 1, because in the vacuum without molecule, the refractivity index is 1, it is not 0.

Similar to the absorption cross section σ with the area dimension, we define a new physical quantity η with the volume dimension to describe the refractive index. We call this quantity as the refraction volume. Therefore, in general speaking, for a molecular system with m electron energy-levels, if the interaction among molecules can be neglected; the total refractive index of the system n is a sum of the refractive index of every electron energy-level n_i plus 1. The refractive index of every electron energy-level n_i is proportional to the molecular number density N_i, the ratio coefficient is the refraction volume η_i of that electron energy-level. Thus the total refractive index of the molecular system can be expressed as

$$n = 1 + \sum_{i=1}^{m} n_i = 1 + \sum_{i=1}^{m} \eta_i N_i, \quad i = 1, 2, 3, \ldots m \tag{7.3.1}$$

where the molecular number density N_i is a function of the light intensity.

Using above five energy-level model in Fig. 7.15, the molecular number densities for the ground state, the singlet and triplet first excited states are denoted by N_1, N_2, and N_3 respectively, and the refraction volumes for the ground state, the singlet and triplet first excited states are denoted by η_0, η_S and η_T respectively, the total refractive index of the system n can be written as

$$n = 1 + \eta_0 N_1 + \eta_{\mathrm{S}} N_2 + \eta_{\mathrm{T}} N_3. \tag{7.3.2}$$

When the incident light is very weak, all of the molecules stay in the ground state, then $N_2 = N_3 = 0$ and $N_1 = N$, the Eq. (7.3.2) becomes

$$n_0 = 1 + \eta_0 N, \tag{7.3.3}$$

where n_0 is the linear refractive index of molecular system, N is the total molecular number density.

As above mentioned in last section, the change of molecular number density of each energy-level with changing the time can be described by the following rate equations:

$$\frac{\partial N_2}{\partial t} = \frac{\sigma_0 I N_1}{\hbar\omega} - \frac{N_2}{\tau_S} - \frac{N_2}{\tau_{ST}}, \tag{7.3.4}$$

$$\frac{\partial N_3}{\partial t} = \frac{N_2}{\tau_{ST}} - \frac{N_3}{\tau_T}, \tag{7.3.5}$$

$$N_1 + N_2 + N_3 = N, \tag{7.3.6}$$

If pulsewidth of the incident laser is much bigger than the all of the energy-level live times of the molecular system, we can regard that the interaction between light and molecular system as a steady-state process. It means $\partial/\partial t = 0$ in the above rate equations, and we don't need to consider the variation of the laser intensity, instead taking its peek intensity of I, we can solve the Eqs. (7.3.4)–(7.3.5) to get the following variables N_1, N_2 and N_3:

$$N_1 = \frac{N}{1 + (A + B)I'}, \tag{7.3.7}$$

$$N_2 = \frac{ANI'}{1 + (A + B)I'}, \tag{7.3.8}$$

$$N_3 = \frac{BNI'}{1 + (A + B)I'}, \tag{7.3.9}$$

where $I' \equiv \frac{I}{I_c}, I_c \equiv \frac{\hbar\omega}{\sigma_0 \tau_S}$ is the saturation intensity, and

$$A \equiv \frac{\tau_{\mathrm{ST}}}{\tau_{\mathrm{ST}} + \tau_{\mathrm{S}}}, \tag{7.3.10}$$

$$B \equiv \frac{\tau_{\mathrm{T}}}{\tau_{\mathrm{ST}} + \tau_{\mathrm{S}}}. \tag{7.3.11}$$

Substituting Eqs. (7.3.7)–(7.3.9) into Eqs. (7.2.3), the total refractive-index of the system can be written as

$$n = 1 + \frac{\eta_0 + (A\eta_{\mathrm{S}} + B\eta_{\mathrm{T}})I'}{1 + (A + B)I'} N. \tag{7.3.12}$$

From Eq. (7.3.12) we can see, when the light is strong enough, not only the ground-state, but also the excited-states in singlet and triplet systems, all have contributions to the total refractive -index of the system. However, when the light is very weak ($I << I_c$) i.e., $I' \to 0$, the total refractive -index then becomes a linear refractive-index, i.e., $n_0 = 1 + \eta_0 N$.

We should say that the contributions of the singlet excited-state and the triplet excited-states to the total refractive index are different. The size of their contribution depends on the parameter values of A and B. From Eqs. (7.3.10) and (7.3.11) we can see, if $\tau_{ST} > > \tau_S$ and τ_T , then $A \approx 1$, and $B \approx 0$. In this case molecules cannot jump to the triplet-state from the singlet-state. The nonlinear refractive index of the system is mainly induced by the singlet first excited-state. The five-level model is degenerated to the three-level model, as shown in Fig. 7.18b. Thus Eq. (7.3.12) becomes

$$n = 1 + \frac{1 + (\eta_S/\eta_0)I'}{1 + I'}\eta_0 N, \tag{7.3.13}$$

where $I' \equiv \frac{I}{I_c}$ and $I_c \equiv \frac{\hbar\omega}{\sigma_0 \tau_S}$.

If $\tau_{ST} < < \tau_S$ and τ_T, then $A \approx 0$ and $B \approx \tau_\mathrm{T}/\tau_S$. In this case, most of molecules transit to the triplet-state from the singlet-state. The nonlinear refractive index of the system is mainly induced by the triplet first excited-state. The five-level model is also degenerated to another three-level model, as shown in Fig. 7.18a. Thus Eq. (7.3.12) becomes

$$n = 1 + \frac{1 + (\eta_\mathrm{T}/\eta_0)I''}{1 + I''}\eta_0 N, \tag{7.3.14}$$

where $I'' \equiv \frac{I}{I'_c}$ and $I'_c \equiv \frac{\hbar\omega}{\sigma_0 \tau_T}$. This formula is suitable for the majority organic materials. We will discuss it below in detail.

Firstly, we discuss the dependent relation of the refractive index with the light intensity. If light is weak, we have $I < < I'_c$, i.e., $I'' < < 1$, the refractive index of the system is a linear refractive index: $n_0 = 1 + \eta_0 N$; if the light is very strong, we have $I > > I'_c$, i.e., $I'' > > 1$, the refractive index is a saturable constant: $n = 1 + \eta_T N$. For the middle saturation, the light intensity is $I = I'_c$, i.e. $I'' = 1$, thus $n = [2 + (\eta_0 + \eta_T)](N/2)$.

Secondly, we discuss that how the ratio (η_T/η_0) affects the refractive index of the system. If $\eta_T < \eta_0$, the system refractive index decreases with the increase of the light intensity, this is the case of the saturation refraction (SR). If $\eta_T > \eta_0$, the system refractive index increases with the increase of the light intensity, this is the reverse saturation refraction (RSR). If $\eta_T < < \eta_0$, Eq. (7.3.14) for expressing the refractive index of the three-level system will be simplified into a saturation equation for expressing the refractive index of the two-level system, that is

$$n = 1 + \frac{\eta_0 N}{1 + \frac{I}{I_c}}. \tag{7.3.15}$$

We can see that the refractive index decreases with the increase of the light intensity.

As a sample, we investigate the C_{60} in toluene solution under the exposure by a laser at wavelength of 532 nm. The solvent toluene is a linear liquid, its refractive index is

$$n_{S0} = 1 + \eta_{S0} N_S, \tag{7.3.16}$$

where η_{S0} and N_S are the fundamental-state refraction volume and total molecular number density of the solution, respectively. Therefore, the linear refractive index of C_{60} in toluene solution under the weak light is

$$n_0 = 1 + \eta_{S0} N_S + \eta_0 N. \tag{7.3.17}$$

According to Eq. (7.3.14), the refractive-index formula of C_{60} in toluene solution is

$$n = n_{S0} + \frac{1 + (\eta_\mathrm{T}/\eta_0)I''}{1 + I''}\eta_0 N. \tag{7.3.18}$$

We take the following data for C_{60} in toluene solution: $\sigma_0 = 2.87 \times 10^{-18}\,\mathrm{cm}^2$, $\sigma_S = 1.57 \times 10^{-17}\,\mathrm{cm}^2$, $\tau_\mathrm{S} = 30\,\mathrm{ns}$, $\tau_\mathrm{T} = 280\,\mu\mathrm{s}$, $\tau_\mathrm{ST} = 1.2\,\mathrm{ns}$, $N = 1.68{\times}10^{18}/\mathrm{cm}^3$, $\eta_0 = 8.44 \times 10^{-22}\,\mathrm{cm}^3$, $I'_c = 460\,\mathrm{W/cm}^2$, to calculate and obtain $n_0 = 1.4984$.

Figure 7.22 presents a group of the curves of the refractive index of C_{60} in toluene solution as a function of the intensity. The curves of 1, 2, 3, 4, 5 are corresponding to $\eta_T = 12.66 \times 10^{-22}\,\mathrm{cm}^3$, $10.55 \times 10^{-22}\,\mathrm{cm}^3$, $8.44 \times 10^{-22}\,\mathrm{cm}^3$, $6.33 \times 10^{-22}\,\mathrm{cm}^3$, $4.22{\times}10^{-22}$ cm or $(\eta_\mathrm{T}/\eta_0) = 1.50, 1.25, 1.00, 0.75, 0.50$. Among these, Curves 1 and 2 belong to $\eta_\mathrm{T} > \eta_0$, i.e., the reverse saturable refraction; Curves 4 and 5 belong to $\eta_\mathrm{T} < \eta_0$, i.e., the saturable refraction; Curve 3 belongs to $\eta_\mathrm{T} = \eta_0$, the refractive index is n_0, which does not change with the optical intensity.

7.3.2 *Physical Significance of Sign Symbol of Nonlinear Refraction Coefficient*

The refractive index of optical Kerr medium can be express as $n = n_0 + \Delta n = n_0 + n_2 I$, where n_2 is nonlinear refraction coefficient. The value of n_2 can be positive or negative for different materials. How to explain the sign symbol of nonlinear refraction coefficient n_2? Now we try to answer this question.

Because $n_0 = 1 + \eta_0 N$ and $n = n_0 + \Delta n$, using Eqs. (7.3.13) and (7.3.14) obtaining from the singlet and triplet models respectively, we can deduce to get the refractive-index change i.e., the nonlinear refractive index of a three-level system:

$$\Delta n = \frac{(\eta_s - \eta_0)NI'}{1 + I'}, \tag{7.3.19}$$

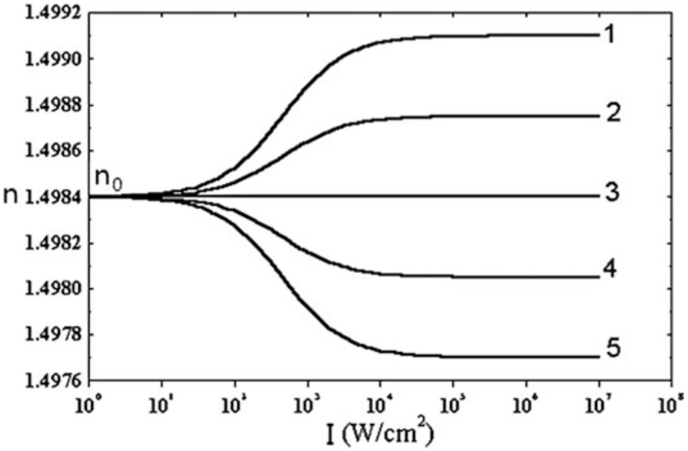


Fig. 7.22 The refractive index as a function of optical intensity for five energy-level of C_{60} in toluene solution, *Curves* of 1, 2, 3, 4, 5 are corresponding to (η_T/η_0) = 1.50, 1.25, 1.00, 0.75, 0.50

$$\Delta n = \frac{(\eta_T - \eta_0)NI''}{1 + I''}. \tag{7.3.20}$$

When $I \ll I_c$, i.e., $I' \ll 1$; or $I \ll I_c'$, i.e., $I'' \ll 1$. Taking Taylor series expansion for Eqs. (7.3.19) and (7.3.20) and only keeping the linear approximation item, the refractive-index change will be

$$\Delta n = \frac{(\eta_S - \eta_0)N}{I_c} I, \tag{7.3.21}$$

$$\Delta n = \frac{(\eta_T - \eta_0)N}{I_c'} I. \tag{7.3.22}$$

Equations (7.3.21) and (7.3.22) show the Kerr effect of the singlet and the triplet system respectively.

Now we obtain the microscopic expressions of nonlinear refraction coefficient n_2, for the singlet system with three-level model, which is

$$n_2 = \frac{(\eta_S - \eta_0)\sigma_0 \tau_S N}{\hbar\omega}; \tag{7.3.23}$$

for the triplet-system with three-level model, which is

$$n_2 = \frac{(\eta_T - \eta_0)\sigma_0 \tau_T N}{\hbar\omega}. \tag{7.3.24}$$

Equations (7.3.23) and (7.3.24) point out that the sign symbol of n_2 depends on the difference between the excited-state refraction volume η_S or η_T and the ground-state refraction volume η_0. If $\eta_S < \eta_0$ or $\eta_T < \eta_0$, namely the system is dominated in the saturable refraction, n_2 is negative; on the contrary, if $\eta_S > \eta_0$ or $\eta_T > \eta_0$, namely the system is dominated in the reverse saturable refraction, n_2 is positive. For example, most of liquid molecular systems far from the resonance belong to the reverse saturable refraction with the positive n_2; however, the compound semiconductors at the exciton-resonance area, such as GaAs, belong to the saturable refraction with the negative n_2. Apparently this judgment should be proved by more experimental results with multiple different materials.

Review Questions of Chapter 7

1. Please deduce the absorption coefficient formula for third-order nonlinear absorption, and explain the relationship between the absorption coefficient and the transmittance of light intensity.
2. What is the two-photon absorption? Please deduce the formula of relationship between two-photon absorption coefficient and the light intensity. How to measure the two-photon absorption coefficient of semiconductor? What is the influence of the free-carrier absorption in this measurement?
3. What is the difference between two nonlinear-refractive-index formulas under two-photon absorption and single-photon absorption (i.e. optical Kerr effect) for the semiconductor?
4. According to two-level and three-level models of molecular systems, to derive the absorption coefficient formulas of the saturated absorption, and explain the reason of absorption-saturation phenomenon in these two molecular models.
5. Why two absorption-coefficient formulas for saturated absorption and third-order nonlinear absorption are different? What the relationship between these two effects is?
6. What is the reverse-saturated absorption? Starting from the five-level model of molecule system to analysis the causes of the saturated absorption; and to deduce the absorption coefficient formula for reverse-saturated absorption under the steady-state condition. Under what conditions the contribution of singlet- or triplet-excited-state absorption is dominate?
7. What is the nonlinear grating-type optical limiter? Please explain the role of reverse-saturated absorption in this limiter.
8. What is the reverse-saturation refraction? Please write down the refractive-index formulas considering the transition between excited states and the linear approximation formula under weak light intensity. From these formulas to explain the physical meaning of the sign symbol of nonlinear refraction coefficient n_2.

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