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NONLINEAR REFRACTION IN MULTILEVEL MOLECULAR SYSTEMS

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The intensity-dependent nonlinear refraction phenomena in a non-resonant multilevel molecular system is studied using rate equations in steady state, including saturable refraction, reverse saturable refraction, and the turnover between these two effects. The relationship between the refraction saturation and the optical Kerr effect is also discussed.

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I. INTRODUCTION

The investigation of nonlinear optics has a 35-year history. Ten years ago, much attention was paid to optical nonlinearities of materials at resonant wavelengths, where there are strong absorption and refraction changes. Many nonlinear optical devices, such as optical bistable devices in semiconductor are based on this principle.[1] However, in these years much attention was focused on organic materials which have a complex molecular structure with multiple energy levels. When organic molecules are irradiated by a strong light, transitions can simultaneously occur from the ground state to the low-excited states and from the low-excited state to the high-excited state. In non-resonant case, the excited-state to excited-state transitions play an important role. Excited-state nonlinear absorption in organic materials has been extensively studied including saturable absorption (SA)[2], reverse saturable absorption (RSA)[3], the turnover from RSA to SA[4] and the turnover from SA to RSA.[5]

The action of strong light not only leads to the change in absorption of the ground state and excited states, but also in refraction of the ground state and excited states according to Kramers-Kronig relation. As we know that many people have expressed the total absorption or total refraction of a multilevel molecular system as a sum of contributions from each energy level and these contributions are all proportional to the population of that level.[6,7]

In this paper, we develop an expression of the total refraction for the multilevel molecular system, and use it to discuss a variety of nonlinear refraction phenomena in a five-level or a four-level molecular system: saturable refraction (SR), reverse saturable refraction (RSR), and the turnover between SR and RSR. We will also point out the relationship between the refraction saturation and optical Kerr effect, and try to know what makes the nonlinear refractive-index coefficient n_2 to be positive or negative.

II. REFRACTIVE INDEX OF FIVE-LEVEL SYSTEM

The energy-level diagram for a five-level molecular system in non-resonant case is shown in Fig.1, in

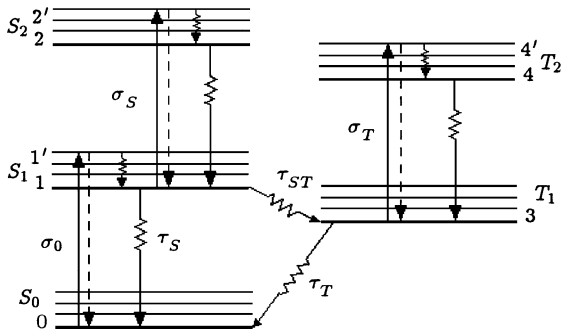


Fig.1. Energy level diagram for an organic molecular system with five electronic levels under a non-resonant excitation.

which 0 denotes the ground-state electronic level, 1 and 2 denote the first and higher singlet excited-state electronic level, 3 and 4 the first and higher triplet excited-state electronic level, respectively; i' denotes a vibronic/rotational higher sublevel of the i-th electronic manifold. When a light with non-resonant frequency ω irradiates the molecular system, the molecules in lowest electronic levels 0, 1, and 3 simultaneously absorb photons in transitions to the sublevels $1'$, $2'$ and $4'$ with absorption cross-sections σ_0, σ_1, and σ_3, respectively. The lifetimes of molecules in sublevels $1'$, $2'$ and $4'$ are very short (less than picosecond). Radiative relaxations of molecules directly from $1'$, $2'$ and $4'$ to 0, 1 and 3 are very weak for organic in room temperature, which could be neglected. Therefore, the only way is through non-radiative relaxation from $1'$, $2'$ and $4'$ to electronic levels 1, 2, and 4, then from 1, 2, and 4 to 0, 1, and 3. The lifetimes in levels 1 and 3 are τ_S and τ_T, respectively; τ_{ST} is

the intersystem-crossing lifetime between 1 and 3.

The energy-level transition in molecules of materials causes the absorption change, as well as the refraction change. The total refractive index of a multilevel molecular system in low-density case is equal to the refractive index of the vacuum plus a linear sum of contributions from the refractive index due to each possible energy-level transition. The refractive index due to each transition is proportional to the population difference between two levels, $N_m - N_n$, where we call the constant of proportionality the refractive volume η_{nm}, because which has a volume dimension. That is,

$$n = 1 + \sum_{n,m} \eta_{nm}(N_m - N_n). \tag{1}$$

In a non-resonant five-level molecular system, the index m denotes the lowest electronic levels 0, 1, or 3; n denotes the sublevels $1'$, $2'$, or $4'$. Because the sublevel populations $N_{1'}, N_{2'}$ and $N_{4'}$ are very small due to short lifetime in these levels, we can neglect these populations and denotes η_{nm} by $\eta_{m'}$. Therefore, we have

$$n = 1 + \sum_m n_m = 1 + \sum_m \eta_m N_m, \tag{2}$$

where n_m is the refractive index of the m-th electronic energy level, m =0, 1, 2, 3, 4. In Eq.(2), the first term is the refractive index in vacuum, the second term is the contribution to the refractive index by each electronic level. When the light intensity is very weak, all molecules stay in the ground state, so that

$$n = 1 + \eta_0 N = n_0, \tag{3}$$

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

If the contributions of the higher lying excited state can be neglected, and the populations of electronic energy levels 0, 1, and 3 are denoted by N_0, N_S, and N_T, the rate equations for the five-level molecular system can be written as

$$\frac{\partial N_S}{\partial t} = \frac{\sigma_0 I}{h\upsilon} N_0 - \frac{N_S}{\tau_S} - \frac{N_S}{\tau_{ST}}, \tag{4}$$

$$\frac{\partial N_T}{\partial t} = \frac{N_S}{\tau_{ST}} - \frac{N_T}{\tau_T}, \tag{5}$$

$$N_0 + N_S + N_T = N, \tag{6}$$

If we use an input laser with a pulse width much longer than the molecular lifetimes, the molecular system can be regarded as in steady state, i.e. $\partial/\partial t = 0$. In addition, we consider the peak intensity of laser pulse only, i.e. the intensity I does not change with time. Using Eqs.(4)–(6), we can solve for the variables N_0, N_S, and N_T as follows

$$N_0 = \frac{N}{1 + (A + B)I'}, \tag{7}$$

$$N_S = \frac{AI'N}{1 + (A + B)I'}, \tag{8}$$

$$N_T = \frac{BI'N}{1 + (A + B)I'}, \tag{9}$$

where $I' \equiv \dfrac{I}{I_S}$ and $I_S \equiv \dfrac{h\upsilon}{\sigma_0 \tau_S}$ is the "saturable intensity", $A \equiv \dfrac{\tau_{ST}}{\tau_{ST} + \tau_S}$ and $B \equiv \dfrac{\tau_T}{\tau_{ST} + \tau_S}$.

According to Eqs.(2), the total refractive index of molecular system is

$$n = 1 + \eta_0 N_0 + \eta_S N_S + \eta_T N_T. \tag{10}$$

Using Eqs.(7)–(9), the total refractive index of system can be written as

$$n = 1 + \frac{\eta_0 + (A\eta_S + B\eta_T)I'}{1 + (A + B)I'} N. \tag{11}$$

One can see that when the light intensity is large enough, not only the ground state, but also the singlet and triplet excited states contribute to the total refraction of the system. However, when $I \ll I_S$, i.e. $I' \to 0$, the total refractive index becomes the linear refractive index, $n = 1 + \eta_0 N = n_0$.

Ⅲ. SATURABLE REFRACTION AND REVERSE SATURABLE REFRACTION

The contribution from the excited singlet and excited triplet are different, it depends on the values of parameters A and B. If $\tau_{ST} \gg \tau_S$ and τ_T, then $A \approx 1$ and $B \approx 0$. In this case, most molecules cannot transfer from the singlet state to triplet excited state. The nonlinear refraction of the system mainly comes from the first excited singlet state. The five-level model reduces to a three-level model. Equation (11) becomes

$$n = 1 + \frac{1 + R_S I'}{1 + I'} \eta_0 N, \tag{12}$$

where $R_S \equiv \dfrac{\eta_S}{\eta_0}$, $I' \equiv \dfrac{I}{I_S}$ and $I_S \equiv \dfrac{h\upsilon}{\sigma_0 \tau_S}$.

If $\tau_{ST} \ll \tau_S$ and τ_T, then $A \approx 0$ and $B \approx \tau_T/\tau_S$. In this case, most molecules can transfer from the singlet state to the triplet excited state. The nonlinear refraction of the system mainly comes from the first triplet excited state. The five-level model also reduces to a three-level model. The Equation (11) becomes

$$n = 1 + \frac{1 + R_T I''}{1 + I''} \eta_0 N, \tag{13}$$

where $R_T \equiv \frac{\eta_T}{\eta_0}$, $I'' \equiv \frac{I}{I'_S}$ and $I'_S \equiv \frac{h\nu}{\sigma_0 \tau_T}$. This formula is applicable to most organic materials and we will discuss it below in detail.

Firstly, we discuss the intensity dependence of refractive index. If the intensity is very small, $I \ll I'_S$, i.e. $I'' \ll 1$, the refractive index of the system is $n = 1 + \eta_0 N = n_0$. On the contrary, if the intensity is very high, $I \gg I'_S$, i.e. $I'' \gg 1$, the refractive index will be a saturated constant value $n = 1 + \eta_T N = n_S$. For the moderate, the intensity $I = I'_S$, i.e. $I'' = 1$, so we have $n = [2 + (\eta_0 + \eta_T)](N/2)$.

Secondly, we discuss how the ratio R_T influences the refractive index of the system. If $\eta_T < \eta_0$ or $|R_T| < 1$, the refractive index decreases with increasing intensity. This is the saturable refraction (SR) case. If $\eta_T > \eta_0$ or $R_T > 1$, the refractive index increases with increasing intensity. This is the reverse saturable refraction (RSR) case.

Finally, if $\eta_T \ll \eta_0$, i.e. $R_T \ll 1$, the refractive-index expression (13) for the three-level system reduces to the formula for the two-level system,

$$n = 1 + \frac{\eta_0 N}{1 + I''}. \tag{14}$$

In order to illustrate SR and RSR, we examine an example of the C_{60} solution in toluene, which is irradiated by a laser beam with wavelength of 532 nm. We take data of C_{60} in toluene solution from Ref.[8]: $\sigma_0 = 2.87 \times 10^{-18}\,\mathrm{cm}^2$, $\sigma_S = 1.57 \times 10^{-17}\,\mathrm{cm}^2$, τ_S=30 ns, τ_T=280 μs, τ_{ST}=1.2 ns, n_0=1.60 and $N = 1.68 \times 10^{18}/\mathrm{cm}^3$. Because the solvent toluene is a linear liquid, the refractive index is $n_{S0} = 1 + \eta_{S0} N_S$, where η_{S0} and N_S are the ground-state refraction volume and the total molecule-number density of solvent, respectively. Equation (13) for C_{60} solution becomes

$$n = n_{S0} + \frac{1 + R_T I''}{1 + I''} \eta_0 N. \tag{13a}$$

The linear refraction of toluene we measured is 1.4970. Under the weak light, the linear refraction of C_{60} solution in toluene is $n_0 = n_{S0} + \eta_0 N$, where n_0=1.4984, $\eta_0 = 8.44 \times 10^{-22}\,\mathrm{cm}^3$. I'_S=460 W/cm^2. A group of corresponding curves of the refractive index n versus intensity I for Eq.(12) is shown in Fig.2. Curves 1, 2, 3, 4, 5 correspond to η_T=12.66, 10.55, 8.44, 6.33, and $4.22 \times 10^{-22}\,\mathrm{cm}^3$, or R_T=1.50, 1.25, 1.00, 0.75, 0.50, respectively. Curves 1 and 2 correspond to R_T >1, i.e. RSR. Curves 4 and 5 are corresponding to R_T <1, i.e. SR. The curve 3 where R_T=1 is corresponding to the linear refraction case for all intensities.

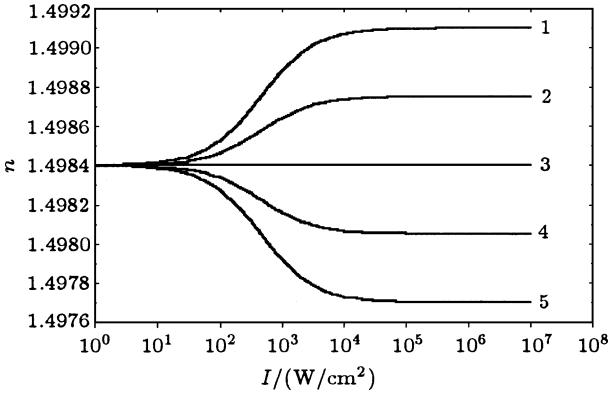


Fig.2. Curves of refractive index versus the intensity of incident light according to Eq.(13) in a 5-level molecular system of C_{60} solution in toluene. Curves 1, 2, 3, 4, 5 correspond to $R_T = \frac{\eta_T}{\eta_0}$=1.50, 1.25, 1.00, 0.75, and 0.50, respectively.

IV. LINEAR APPROXIMATION OF REFRACTION SATURATION

The refractive index of the molecular system can be written as $n = n_0 + \Delta n$, where the nonlinear refractive index Δn is a function of the intensity. According to Eq.(12) for the refractive index of the singlet three-level system, we have

$$\Delta n = \frac{(\eta_S - \eta_0) N I'}{1 + I'}. \tag{15}$$

Similarly, for the triplet three-level system we have

$$\Delta n = \frac{(\eta_T - \eta_0) N I''}{1 + I''}. \tag{16}$$

When $I \ll I_S$, i.e. $I' \ll 1$, or $I \ll I'_S$, i.e. $I'' \ll 1$, the nonlinear refractive index of the system can be written as

$$\Delta n = \frac{(\eta_S - \eta_0) N}{I_S} I, \tag{17}$$

or

$$\Delta n = \frac{(\eta_T - \eta_0) N}{I'_S} I. \tag{18}$$

Therefore, we obtain the familiar linear dependence on intensity of the optical Kerr effect,

$$n = n_0 + n_2 I, \tag{19}$$

where n_2 is called the Kerr nonlinear refractive coefficient. Therefore, the Kerr effect is a linear approximation to the nonlinear refractive index valid at low intensities. Using Eqs.(12) and (13), we have

$$n_2 = \frac{(\eta_S - \eta_0) \sigma_0 \tau_S N}{h\nu}, \tag{20}$$

or

$$n_2 = \frac{(\eta_T - \eta_0) \sigma_0 \tau_T N}{h\nu}. \tag{21}$$

Formulas (20) and (21) are microscopic expressions for the nonlinear refractive coefficient. They show that the sign of n_2 depends on the difference of the excited-state refraction volume η_S or η_T with that of the ground-state refraction volume η_0. If $\eta_S - \eta_0 < 0$ or $\eta_T - \eta_0 < 0$, i.e. the system is in SR, n_2 is negative; If $\eta_S - \eta_0 > 0$ or $\eta_T - \eta_0 > 0$, i.e. the system is in RSR, then n_2 is positive. For a certain photon energy, the numerical value of n_2 is proportional to $|\eta_i - \eta_0|$ (η_i is excited-state refraction volume), the ground-state absorption $\sigma_0 N$ and the excited-state lifetime τ_S or τ_T.

V. TRANSITION BETWEEN SR AND RSR

Now we discuss the influence of higher exited states on the nonlinear refraction of the molecular system. For simplicity, we consider a singlet-four-level molecular system, as shown in Fig.3, and suppose the

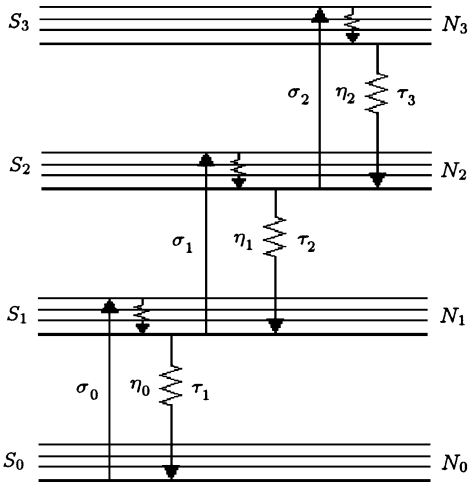


Fig.3. Singlet-four-level molecular system used to investigate the effect of higher lying excited state on the refractive index.

incident laser with a pulse width much shorter than the intersystem lifetime. The rate equations for the populations N_0, N_1 and N_2 in levels S_0, S_1, and S_2 (N_3 in S_3 and populations in sublevels are neglected) are

$$\frac{\partial N_1}{\partial t} = \frac{\sigma_0 I}{h\nu} N_0 - \frac{\sigma_1 I}{h\nu} N_1 - \frac{N_1}{\tau_1} + \frac{N_2}{\tau_2}, \tag{22}$$

$$\frac{\partial N_2}{\partial t} = \frac{\sigma_1 I}{h\nu} N_1 - \frac{N_2}{\tau_2}, \tag{23}$$

$$N_1 + N_1 + N_2 = N. \tag{24}$$

In the steady-state case, i.e. $\frac{\partial N_1}{\partial t} = \frac{\partial N_2}{\partial t} = 0$, we get

$$N_0 = \frac{1}{1 + I' + I'I''} N, \tag{25}$$

$$N_1 = \frac{I'}{1 + I' + I'I''} N, \tag{26}$$

$$N_2 = \frac{I'I''}{1 + I' + I'I''} N, \tag{27}$$

where $I' \equiv \frac{I}{I_{S_1}}$, $I_{S_1} \equiv \frac{h\nu}{\sigma_0 \tau_1}$; $I'' \equiv \frac{I}{I_{S_2}}$, $I_{S_2} \equiv \frac{h\nu}{\sigma_1 \tau_2}$
The total refractive index is

$$n = 1 + \eta_0 N_0 + \eta_1 N_1 + \eta_2 N_2. \tag{28}$$

The levels S_0, S_1 and S_2 all contribute to the total refractive index of the system. Substituting Eqs.(25)–(27) into Eq.(28), we have

$$n = 1 + \left[\frac{1 + R_1 I' + R_2 I' I''}{1 + I' + I' I''} \right] \eta_0 N, \tag{29}$$

where $R_1 = \frac{\eta_1}{\eta_0}$, $R_2 = \frac{\eta_2}{\eta_0}$, and $n_0 = 1 + \eta_0 N$. The nonlinear refractive index $\Delta n = n - n_0$ is

$$\Delta n = \frac{(\eta_1 - \eta_0) I' + (\eta_2 - \eta_0) I' I''}{1 + I' + I' I''} N. \tag{30}$$

Figure shows curves of n as functions of input intensity I according to Eq.(29) in C_{60}/toluene solution with same data as the above sample: $\sigma_0 = 2.87 \times 10^{-18}\,\mathrm{cm}^2$, $\sigma_1 = 1.57 \times 10^{-17}\,\mathrm{cm}^2$, τ_1=30 ns, τ_2=10 ps, $N = 1.68 \times 10^{18}/\mathrm{cm}^3$, N_{S0}=1.4970, n_0=1.4984 and $\eta_0 = 8.44 \times 10^{-22}\,\mathrm{cm}^3$. Curves 1, 2, 3, 4, 5 correspond to $R_1 = \frac{\eta_1}{\eta_0}$=1.50, 1.25, 1.00, 0.75, 0.50 and $R_2 = \frac{\eta_2}{\eta_0}$=0.50, 0.75, 1.00, 1.25, 1.50, respectively. If $\eta_1 < \eta_0 < \eta_2$, n changes from SR to RSR (curves 1 and 2); if $\eta_1 > \eta_0 > \eta_2$, then n changes from RSR to SR (curves 4 and 5). If $\eta_0 = \eta_1 = \eta_2$, $n = 1 + \eta_0 N = n_0$, n is independent of intensity (curve 3). Here we should mention that Fig.4 is only a theoretical result. Actually, the material will be damaged when the intensity is larger than $10^9\,\mathrm{W/cm}^2$.

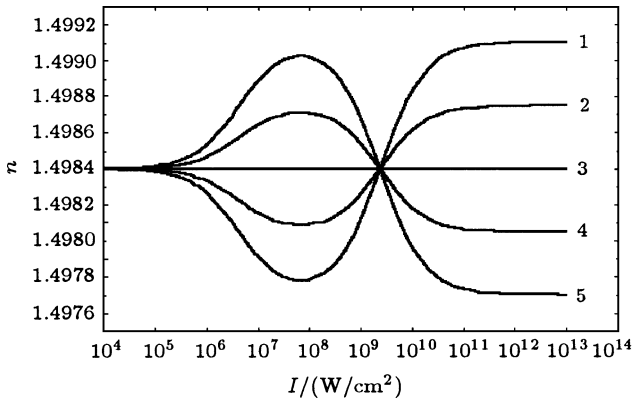


Fig.4. Curves of refractive index versus the intensity of incident light according to Eq.(29) in 4-level molecular system of C_{60}. Curves 1, 2, 3, 4, 5 correspond to $R_1 = \frac{\eta_1}{\eta_0}$=1.50, 1.25, 1.00, 0.75, 0.50 and $R_2 = \frac{\eta_2}{\eta_0}$=0.50, 0.75, 1.00, 1.25, 1.50, respectively. Curves 1 and 2 correspond to $\eta_1 < \eta_0 < \eta_2$, i.e. SR turns into RSR. Curves 3 and 4 correspond to $\eta_1 > \eta_0 > \eta_2$, i.e. RSA turns into SA. Curve 3 corresponds to $\eta_0 = \eta_1 = \eta_2$, where $n = n_0$.

VI. CONCLUSION

We have systematically studied the steady-state properties of nonlinear refraction in a five-level molecular system or a four-level system. It is pointed out that in low-density case, the total refractive index is equal to a linear sum of refractive indexes in each level plus the refractive index of the vacuum. The contribution to the refractive index of each level is equal to the product of the refraction volume and the population of that level. In non-resonant case, the refraction volume of the excited state is larger than that of the ground state. Therefore, the excited-state refraction strongly contributes to the total refraction of system. For most organic molecular system, the triplet first exited state plays an especially important role.

The refractive index of a molecular system under the action of a strong laser can be saturated or reversibly saturated. When the effect of higher lying levels cannot be neglected, the refractive index of the system can switch between saturation and reverse saturation under certain conditions.

The "optical Kerr effect" is a low-level approximation to saturable refraction or reverse saturable refraction. We have presented two microscopic expressions for the nonlinear refractive coefficient n_2 in singlet and triplet molecular systems, respectively. They show that for the organic solution, the sign and the numerical value of n_2 mainly depend on the difference between the excited-state refraction volume and the ground-state refraction volume. The above conclusions need be proved by further experiments.

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