

Optical limiting in polar macromolecules in the nanosecond time range

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The optical limiting by resonant two-photon absorption in polar media, such as some conjugated organic compounds with large polarizable π -electron system and biopolymers, is studied in terms of a three-level mixed-parity molecular system upon nanosecond laser irradiation. The two-photon absorption of polar medium is calculated and its effect on the transmitted laser intensity is analyzed. The numerical results indicate the dependence of the optical limiting efficiency on the magnitude of the permanent dipole moments of the electronic molecular states involved in nonlinear optical interaction between the laser electro-magnetic field and polar macromolecules.

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1. Introduction

The importance of the human eye and optical sensors protection against intense light motivates the research on the optical power limiting. Based on various mechanisms, this effect strongly depends on the optical nonlinearity of the media and is well established in organics, fullerenes, semiconductors, semiconductor nanoparticles, polymers and other materials [1]. The two-photon-absorption (TPA)-induced optical limiting has been object of intensive investigations [2,3]. Since it is determined by the third-order nonlinear optical (NLO) susceptibility $\chi^{(3)}$ of the medium, of special interest are substances having high $\chi^{(3)}$ and resonantly enhanced $\chi^{(3)}$.

The highly dipolar media are materials which properties are desirable for TPA-induced optical limiting. They consist of molecules with large permanent dipole moments [4], as well as nonzero differences of the permanent dipole moments ($\Delta\mu$) for vibronic transitions [5], e.g. compounds possessing a linear conjugated 6π electron system and metal-organic complexes. Some macromolecules have extremely large permanent dipole moments in solutions, like acetylcholinesterase [6], collagene [7] and other biomolecular complexes and biopolymers.

It is well established that the large permanent dipole moments can considerably enhance the NLO properties of polar media [8-10]. In particular, the role of the permanent dipole moments and $\Delta\mu$ in TPA in a two-level quantum system having $\Delta\mu \neq 0$ has been analyzed for electronic spectra [5,11,12]. Attractive as optical limiters are materials not only with large permanent dipole moments,

but also with a large $\Delta\mu$. Here we have studied optical limiting by two-photon resonant activation of such materials containing polar macromolecules by nanosecond high-intensity ($>10^8$ W/cm²) laser pulses. The macromolecular media have been modeled by a three-level quantum system which is more realistic than the two-levels one.

2. Model of optical limiting by TPA in a three-level polar molecule

The TPA-induced optical power limiting [1,2,13] is defined by the macroscopic cubic NLO susceptibility $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ which imaginary part is directly related to the TPA coefficient $\beta^{(2)}$ [14]:

$$\beta^{(2)} = 8\pi^2 \text{Im} \chi^{(3)}(-\omega; \omega, -\omega, \omega) \omega [c^2 \varepsilon]^{-1} \quad (1)$$

where ε is the dielectric constant of the medium at the frequency ω . The transmitted intensity (I) of a laser beam with a Gaussian spatial profile and frequency ω propagating through a medium with no linear attenuation, is given by [14]:

$$I(L) = I_0 (1 + I_0 \beta^{(2)} L)^{-1} \quad (2)$$

where L is the effective NLO-interaction length (the thickness of the material), and I_0 is the input intensity. This expression agrees very well with experimental data [1,2,13].

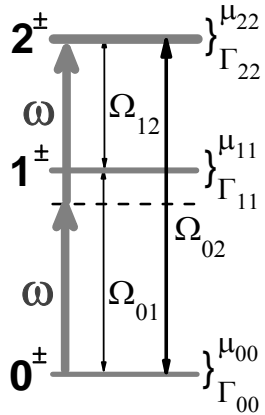


Fig. 1. Schematic three-level polar molecular system. For a resonant TPA, two incident photons (2ω) approach the two-photon resonance at Ω_{02} .

In the present work, $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ was calculated by the density-matrix formalism (perturbative expansion) [14] as described in details in [10]. A three-level mixed-parity (\pm) molecular system (Fig. 1) was considered, where the levels 0,1,2 correspond to electronic states of organic molecule: S_0 (ground state) and excited S_1 and S_2 states with permanent dipole moments μ_{ij} and population decay rates Γ_{ij} ($i = 0, 1, 2$).

Let us assume: (i) an aligned medium and transition dipoles to be along a major molecular axis, i.e. parallel transition dipoles, $\mu_{01} \parallel \mu_{12} \parallel \mu_{02}$, and, moreover (ii), that the molecules have a preferred orientation of the permanent dipole moment presumably aligned along the same axis for symmetry reasons. These assumptions should be done for the sake of concreteness of the interpretation of the role of $\Delta\mu$ (if the dipoles are randomly aligned, an averaging using the statistical distribution of the dipole orientation is necessary). Consider also the laser polarization direction along the major molecular axis, i.e. the vectors μ and $\Delta\mu$ lying along that polarization, otherwise only the components of μ and $\Delta\mu$ on the laser polarization direction should be taken into account. As it is known, when the molecules have a large PDM, the interaction of the electric field of the laser irradiation with the dipoles leads to their partial orientation. The dipole reorientation of large molecules depends on steric hindrance and is still possible during the nanosecond regime of laser excitation (≥ 1 ns). If we suppose transition dipoles with similar values, $\mu_{01} \approx \mu_{12} \approx \mu_{02} = \mu$, then the expression obtained for $\chi^{(3)}$ can be written as:

$$\chi^{(3)}(-\omega; \omega, -\omega, \omega) = \frac{N}{6\hbar^3} \mu^4 L_f R(\omega) \quad (3)$$

where N is the number of molecules per unit volume, $L_f = [(n_0^2 + 2)/3]^4 \sim 4$ is the local field correction to $\chi^{(3)}$ (Lorentz-type approximation) [14], the linear index of refraction is $n_0 = 1.5$.

Our result for the resonant term $R(\omega)$ in Eq. (3) obtained by expansion of density-matrix can be expressed as

$$R(\omega) = \chi_{02}'' \left[\begin{aligned} & (\chi_{02}'^2 + \chi_{02}' \chi_{22}) \xi^2 + \\ & + (\chi_{01} \chi_{22} + 2\chi_{01} \chi_{02}' - \chi_{02}' \chi_{12}) \xi + \\ & + (\chi_{01}'^2 - \chi_{01} \chi_{12}) \end{aligned} \right] \quad (4)$$

with individual terms:

$$\begin{aligned} \chi_{01} &= (\Omega_{01} - \omega - i\Gamma_{01})^{-1} \\ \chi_{02}' &= (\Omega_{02} - \omega - i\Gamma_{02})^{-1} \\ \chi_{02}'' &= (\Omega_{02} - 2\omega - i\Gamma_{02})^{-1} \\ \chi_{12} &= (\Omega_{12} - \omega - i\Gamma_{12})^{-1} \\ \chi_{22} &= (\omega + i\Gamma_{22})^{-1} \end{aligned} \quad (5)$$

Here, Ω_{ij} and Γ_{ij} are the frequency and relaxation constant of $i \rightarrow j$ transition, respectively ($i, j = 0, 1, 2$). The dimensionless parameter $\xi = \Delta\mu/\mu$ includes the difference $\Delta\mu = \mu_{22} - \mu_{00}$ relevant to TPA at Ω_{02} .

3. Results and discussion

In the calculations, we used moderate values $\mu = 1$ Debye for the transition dipole moments in Eq. (3), and $\Delta\mu$ were varied in the range from 1 to 20. Such values are similar to those of some organic and polymeric materials known as polar media [8,12,15]. For instance, $\Delta\mu = 13$ D has been measured as a difference between the ground and first excited state of retinal [16]. As for as the frequency parameters, reasonable values were used which are typical for an organic molecule with vibronic transitions: $\Omega_{02} = 25000 \text{ cm}^{-1}$, $\Omega_{01} = 15000 \text{ cm}^{-1}$ (Fig. 1), $\Gamma_{ij} = 100 \text{ cm}^{-1}$, $\Gamma_{ii} = 10 \text{ cm}^{-1}$ ($i, j = 0, 1, 2$). The other parameters: $L = 1$ mm which is of practical importance, $n_0 = 1.5$ and $N = 10^{18} \text{ cm}^{-3}$ corresponding to condensed phase. The large molecules with large permanent dipole moments have been known to tend to aggregation at high concentration, especially the rod-like ones.

The contribution of the difference $\Delta\mu$ of the permanent dipole moments to TPA can be distinguish comparing $\text{Im}\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ calculated by Eqs. (3), (4) and (5) for $\xi \neq 0$ and $\xi = 0$. Fig. 2 depicts the spectra $\beta^{(2)}(\delta)$, where $\delta = 2\omega - \Omega_{02}$ is the detuning from the two-photon resonance. Similarly to the two-level polar molecule [11], the effect of enhancement of TPA due to $\Delta\mu$ is existing also in resonant TPA described by a three-level model. In fact, two-photon transitions between two states (in our case 0 and 2) of mixed parity are possible only when the difference between their permanent dipole moments is nonzero. Formally, the presence of a third intermediate

level leads to additional terms in the expression for $\chi^{(3)}(-\omega; \omega, \omega, -\omega, \omega)$ (Eqs. (3), (4), (5)). Actually, this molecular state could also resonantly enhance the TPA.

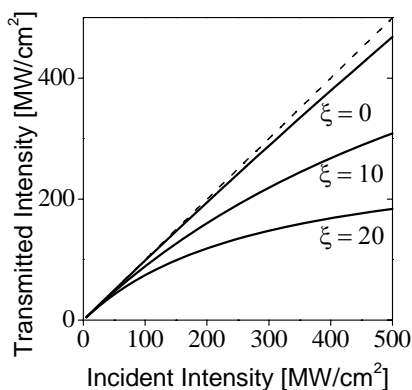


Fig. 2. TPA coefficient $\beta^{(2)}$ of polar molecule calculated around the two-photon resonance Ω_{02} for various $\xi = \Delta\mu/\mu$. $\Gamma = \Gamma_{02}$ is the spectral width (HWHM) of the two-photon resonance.

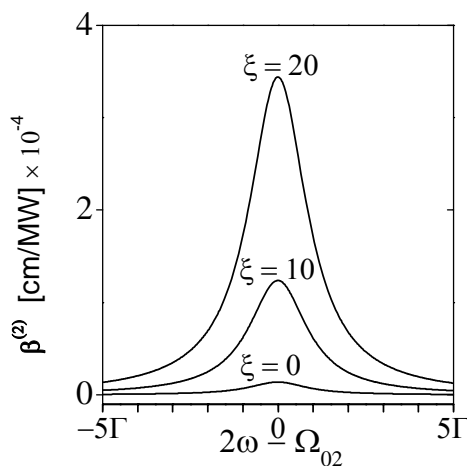


Fig. 3. Transmitted intensity I versus input intensity I_0 calculated for various $\xi = \Delta\mu/\mu$. Dashed line – the transmittance of a transparent linear medium.

Fig. 3 illustrates the numerical results for the transmitted intensity as a function of the incident intensity of a laser beam passed through a polar medium and undergoing TPA. The intensity range of $I_0 = 0 - 500$ MW/cm^2 available by commonly used high-power nanosecond and sub-nanosecond laser sources, is considered. The dependencies presented are computed using Eq. (2) for three values of $\xi = \Delta\mu/\mu$. As seen from Fig. 3, the TPA activation alters the transmittance of the polar medium. Comparing to the case of a transparent linear medium (dashed line), the transmittance is

appreciably affected by the difference $\Delta\mu$ of the permanent dipole moments of electronic states coupled by the two-photon resonance. Thus, the material can be transparent at low I_0 until a predetermined threshold intensity level above which the transmitted light remains limited. The reference to the most efficient power-limiting effects reported for fullerene-containing media [13] and chitosane solutions [17] having other optical limiting mechanisms (reverse saturable absorption and nonlinear refraction), as well as the two-photon resonant enhancement of $\beta^{(2)}$ in polydiacetylene poly-4BCMU gels [18] and organic molecule-doped solid materials [2], indicate the relatively good optical limiting performance of the polar media under two-photon resonance conditions and, therefore their potential for optical limiting application.

4. Conclusions

We have analyzed the nonlinear absorption of intense nanosecond laser pulses in compounds with large permanent dipole moments. The result shows that the resonant two-photon absorption can significantly limit the intensity of laser beam propagating through such media. This effect depends on the difference between the permanent dipole moments of the ground and two-photon-excited electronic molecular state.

The highly dipolar molecules can be incorporated into solid matrix in order to be useful for various optical limiting applications. The intensity-dependent two-photon absorptive properties of such materials could be attractive for products as optical films for protection toward intense laser aggressions, as well as for functional devices, e.g. optical switches.

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