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NONLINEAR OPTICAL MATERIALS: NONLINEAR REFLECTION IN COMPOUNDS WITH LARGE PERMANENT DIPOLE MOMENTS

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We have analyzed the possibility of enhancing the nonlinear reflection of coherent optical waves in materials with large permanent dipole moments, e.g. some conjugated organic compounds. The theoretical results indicate that phase-conjugate reflection in modified four-wave mixing $\omega = \omega + \omega - \omega$ is enhanced by up to several orders of magnitude, if proper two-photon resonances at 2ω are achieved in such nonlinear optical media. This effect mainly depends on the difference between the permanent dipole moments of the molecular states involved in the relevant nonlinear process.

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1. Introduction

Among the promising materials for nonlinear optical (NLO) applications are the so called polar media defined as compounds with mixed-parity states - states with permanent dipole moments. Many molecules have such permanent dipoles [1 -3] and nonzero differences of the permanent dipole moments ($\Delta\mu$), e.g. compounds possessing a linear conjugated 6π electron system have $\Delta\mu \neq 0$ for some vibronic transitions [2]. Especially attractive as advanced NLO materials are substances with large permanent dipole moments, as well as a large $\Delta\mu$.

It is of importance to take the permanent dipole moments and $\Delta\mu$ into account in the NLO processes. Various types of NLO phenomena have been studied in polar media, for example, two-photon radiative processes [4], two-photon absorption and four-wave mixing (FWM) [5, 6] in a two-level quantum system, where the contribution of $\Delta\mu$ between the molecular states involved in a two-photon resonance (TPR) to the two-photon cross section is large.

TPR phase conjugation by means of FWM in a two-level polar system was also studied [7, 8]. In a three-level quantum system, the role of $\Delta\mu$ on the third-order optical nonlinearity of polar media was modelled for off-resonant FWM [9]. Here we analyze the effect of $\Delta\mu$ on the phase-conjugate reflection by FWM $\omega = \omega + \omega - \omega$ at TPR 2ω in a three-level mixed-parity quantum system. The nanosecond regime of excitation is considered.

2. Model of phase-conjugate reflection in a three-level polar molecule

A phase-conjugate wave can be generated with the FWM system shown in Fig.1(a). Three coherent light waves of the same frequency ω take part in this NLO interaction [10]. They have different propagation directions - two oppositely-travelling strong pump waves $\boldsymbol{E}_1$ and $\boldsymbol{E}_2$, and a

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probe wave $\boldsymbol{E}_{\mathbf{P}}$. The generated phase-conjugated wave $\boldsymbol{E}_{\mathbf{PC}}$ is coherent because the phase-matching condition is automatically fulfilled. The process is described by a third-order NLO susceptibility

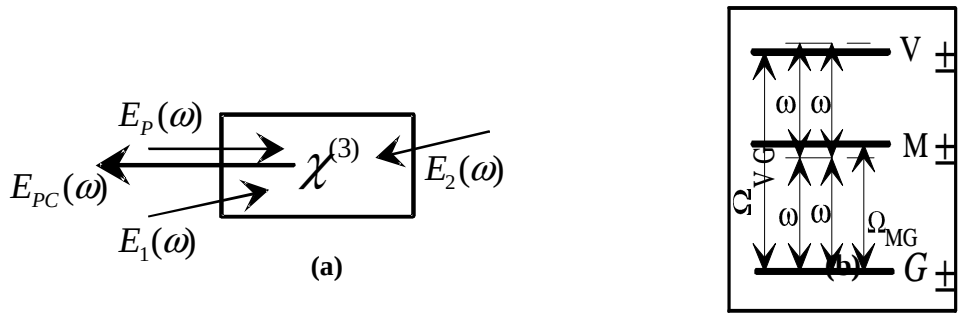

Fig.1. (a) - Scheme of phase-conjugation by FWM $\omega = \omega + \omega - \omega$.
(b) - Energy-level diagram of a three-level polar system.

$\chi^{(3)}(\omega = \omega + \omega - \omega)$ and is well established in the non-resonance case [11], for single-photon resonance [12], as well as TPR [13]. The phase-conjugate reflection spectrum is:

$$R = \frac{\left| q \sin(WL) \right|^2}{\left| W \cos(WL) + \mathrm{Re}\{\alpha\} \sin(WL) \right|^2} \quad , \quad \text{where} \quad W^2 = \left| q \right|^2 - (\mathrm{Re}\{\alpha\})^2 \tag{1}$$

In Eq. (1), α accounts for the absorption, and L is the effective interaction length. For parallel polarized waves, $\boldsymbol{E}_1$, $\boldsymbol{E}_2$, $\boldsymbol{E}_P$, $\boldsymbol{E}_{PC}$, and for $|\boldsymbol{E}_1| = |\boldsymbol{E}_2|$, one can write

$$\alpha = -i\, 2I\chi^{(3)}(\omega = \omega + \omega - \omega) \qquad \text{and} \qquad q = -I\chi^{(3)}(\omega = \omega + \omega - \omega) \tag{2}$$

where $I = (2\pi\omega/cn)A^2$, A is the laser wave amplitude, n is the refractive index of the media, and c is the velocity of light. In Eqs.2, $\chi^{(3)}$ is the macroscopic cubic optical susceptibility, in our case that of a polar molecule. These complex characteristics strongly depend on the presence of resonances and their satisfaction in the system.

Fig.1(b) depicts the energy-level diagram of a three-level polar system and FWM $\omega = \omega + \omega - \omega$ under the TPR condition $\omega + \omega \rightarrow \Omega_{TPR} = \Omega_{VG}$. To calculate $\chi^{(3)}(\omega = \omega + \omega - \omega)$, the density-matrix formalism is used [9]. Assuming that the transition dipole moments have similar values, $\mu_{VG} \sim \mu_{VM} \sim \mu_{MG}$, the expression for $\chi^{(3)}$ can be simplified as:

$$\chi^{(3)}(\omega = \omega + \omega - \omega) = \frac{N}{6\hbar}\frac{\mu^4}{D_{VG}(2\omega)} \times \left[\begin{array}{l} \dfrac{1}{D_{MG}(\omega)}\left(\dfrac{1}{D_{MG}(\omega)} - \dfrac{1}{D_{VM}(\omega)} \right) + \\ \\ + \xi \left(\dfrac{1}{D_{MG}(\omega) D_{VV}^*(-\omega)} + \dfrac{2}{D_{VG}(\omega) D_{MG}(\omega)} - \right. \\ \\ \left. - \dfrac{1}{D_{VG}(\omega) D_{VM}(\omega)} \right) + \\ \\ + \dfrac{\xi^2}{D_{VG}(\omega)} \left(\dfrac{1}{D_{VV}^*(-\omega)} + \dfrac{1}{D_{VG}(\omega)} \right) \end{array} \right] \tag{3}$$

In this expression, the $\Delta\mu$ relevant to the two-photon transition at Ω_{TPR} is included through the parameter $\xi = \Delta\mu/\mu$, where μ stands for μ_{ij} (i, j = G, M, V). N is the particle density, $D_{ij}(\varpi) = \omega_{ij} - \varpi - i\Gamma_{ij}$, ($\varpi = \omega; 2\omega$), where ω_{ij} and Γ_{ij} are the frequency and relaxation constant of the transition $i \rightarrow j$, respectively, and Γ_{ii} is the population decay rate.

3. Results and discussion

Fig. 2 illustrates the phase-conjugate reflection spectra $R(\delta)$ computed in the vicinity of the two-photon resonance; $\delta = (2\omega - \omega_{TPR})/\Gamma_{VG}$. In the calculations, the laser amplitude is fixed to a moderate value $A = 2 \times 10^2$ esu, and $n = 1.5$, $L = 0.5$ cm, $N = 3 \times 10^{21}$ cm^{-3} (condensed phase). Reasonable system parameters corresponding to an organic molecule with vibronic transitions $\Omega_{VG} = \Omega_{TPR} = 25000$ cm^{-1}, $\Omega_{MG} = 15000$ cm^{-1}, Γ_{ij}=100 cm^{-1}, $\Gamma_{ii} = 10$ cm^{-1} (i, j = G, M, V) are selected. The values of $\xi = \Delta\mu/\mu$ in our model are close to those of various organic and polymeric materials, particularly polar media where $|\xi|$ is in the range 0.1 to 20 [1, 3, 6, 7, 14, 15, 16].

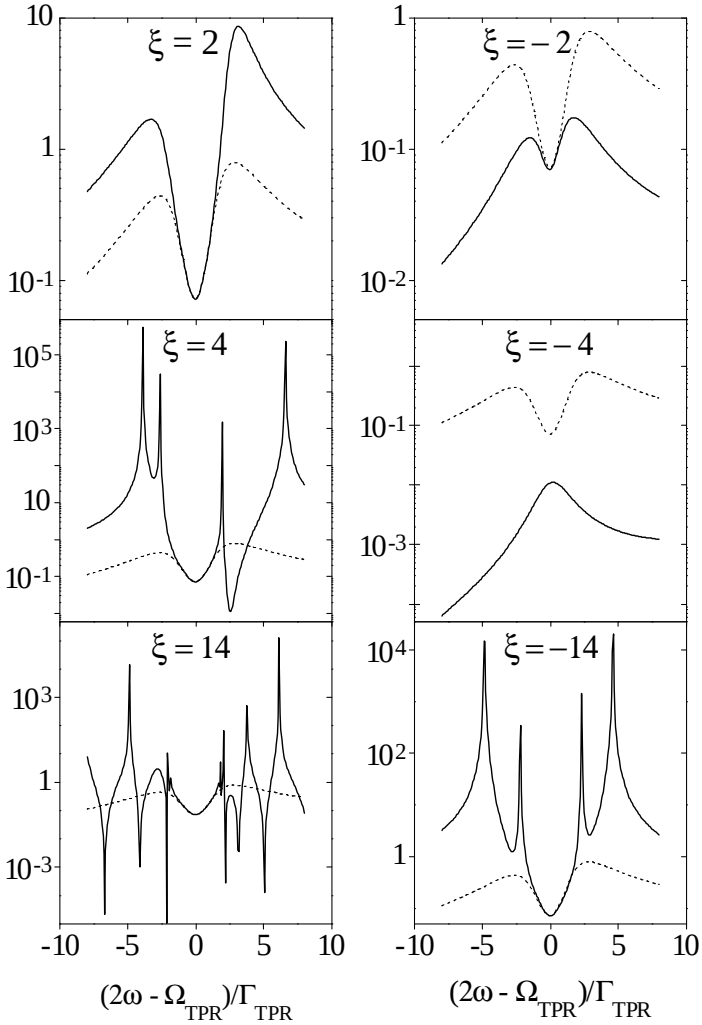

Fig. 2. Numerical results for the phase-conjugate reflectivity R for various values of $\xi=\Delta\mu/\mu$. The dashed line shows R for a corresponding non-polar molecule ($\Delta\mu = 0$), for comparison.

Comparison of $R(\delta)$ for the case of a non-polar system ($\Delta\mu = 0$, dashed lines) with the case of a polar one (with two-photon transition between states having $\Delta\mu \neq 0$, solid lines) shows that the

contribution of $\Delta\mu$ to $\chi^{(3)}(\omega = \omega + \omega - \omega)$ strongly influences the spectrum $R(\delta)$. The effect depends on both the magnitude and sign of $\Delta\mu$, as follows from Eq. 3. A considerable enhancement is possible in the off-resonant region. In some cases, the value of R could be very high - R is enhanced by up to several orders of magnitude in comparison to the corresponding non-polar system. The spectral distribution of the generated coherent signal also undergoes appreciable changes - the spectral maxima are shifted from the exact resonance, in agreement with [17].

4. Conclusions

The spectra of nonlinear optical reflections generated by phase-conjugate optical four-wave mixing $\omega = \omega + \omega - \omega$ under two-photon resonance at 2ω in polar molecules are modelled. It is shown numerically that an enhancement of the phase-conjugate reflectivity can be obtained in such media. This effect depends on the difference between the permanent dipole moments of both molecular states coupled by the two-photon resonance at 2ω.

The advantage of two-photon-resonant phase-conjugate reflection in polar media is the possibility to obtain much higher (several orders of magnitude) reflection than in non-polar ones, for an equal laser intensity and identical other conditions.

This result is useful in materials science and engineering, e.g. for developing systems (conjugated organic compounds having an appropriate $\Delta\mu/\mu$ and suitable two-photon resonances) with a sufficient two-photon-resonant FWM response at $\omega = \omega + \omega - \omega$, attractive for phase-conjugation applications and the design of devices working in such a regime.

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