

Anti-Stokes femtosecond photon echo in a polymer film

S.V. Petrushkin, V.V. Samartsev

Abstract. An anti-Stokes model is proposed which explains the room-temperature blue shift of the echo-signal spectrum compared to the spectrum of exciting femtosecond pulses in a polymer film doped with dye molecules. The possibility of realising the anti-Stokes regime of coherent laser cooling of such films is analysed.

Keywords: photon echo, femtosecond pulses, optical cooling.

1. Introduction

In [1, 2], femtosecond photon-echo signals were studied experimentally at room temperature in a polymer film doped with dye molecules. In particular, it was found that echo-signal spectra are shifted to the blue compared to the spectra of exciting pulses. In this paper, we propose the anti-Stokes model explaining previous femtosecond photon echo experiments [1–3] with a polyvinyl butyral film doped with phthalocyanine molecules.

The spectrum of primary femtosecond photon echo taken from [1–3] is shown in Fig. 1. One can see that this spectrum is shifted to the blue by 3.5 nm (60 cm^{-1}) compared to the excitation spectrum. This means that the echo-photon energy exceeds the excitation-photon energy by the energy of a phonon involved in the electron–phonon excitation of an impurity dye molecule. The inhomogeneous width of the $S_0 \rightarrow S_1$ absorption band is 22 nm (370 cm^{-1}) [4], while the homogeneous width achieves $5 \times 10^{12} \text{ Hz}$ [1, 2]. Recall that phthalocyanine molecules (at the concentration $10^{-3} - 10^{-4} \text{ M}$) were excited by 793-nm, 65-fs pulses from a Ti:sapphire laser.

Note that at present considerable efforts are made to create a solid-state laser refrigerator [5, 6] for cooling condensed media from room to liquid nitrogen and even liquid helium temperatures. To be competitive with Peltier coolers, such laser refrigerators should be miniature, simple,

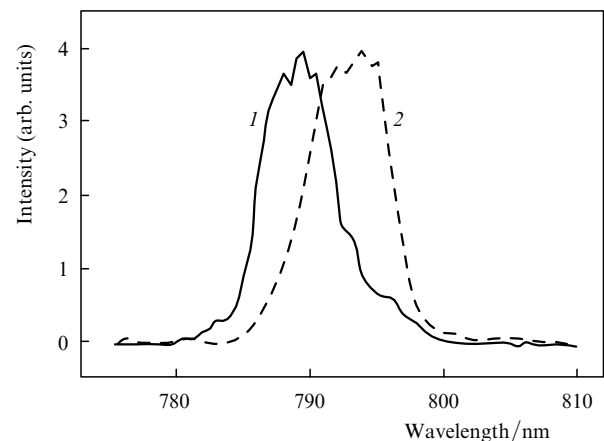


Figure 1. Room-temperature spectrum of the primary echo in a polymer film doped with dye molecules (1) and the excitation signal transmitted through the film (2).

and low-cost. Because most of the proposed schemes of laser refrigerators are incoherent, the cooling intensity is proportional to the number N of impurity atoms [6]. The exception is the scheme based on the optical superradiance regime [7]. In this paper, we propose a new anti-Stokes regime of coherent laser cooling with the intensity proportional to the square N^2 of the number of active impurity molecules. The concept of this cooling regime appeared due to analysis of the above experimental studies of the spectra of a femtosecond photon echo in a polymer film.

2. The anti-Stokes model of a femtosecond photon echo

Molecules in amorphous matrices are similar in many respects to impurity centres in crystals. It is assumed usually that the electronic excitation energy of a polymer film greatly exceeds the electronic excitation energy of impurity molecules. Therefore, laser pulses in the spectral region of interest to us interact only with impurity molecules. The interaction between molecules themselves is neglected by assuming that the concentration of molecules is low enough.

The shape of the spectrum of impurity molecules is determined by the vibronic and electron–phonon interaction. The vibronic interaction is caused by the interaction of the electron motion in a molecule with intramolecular vibrations, while the electron–phonon interaction is determined by the interaction of the electron motion in a

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molecule with intermolecular vibrations of an amorphous matrix. The shape of spectral bands is determined by the electron–phonon interaction. It is known [8] that the absorption band of impurity molecules in an amorphous matrix consists of a narrow zero-phonon line (ZPL) of the Lorentzian shape, corresponding to transitions in molecules without a change of matrix phonons, and of a broad phonon sideband (PSB) corresponding to transitions accompanied by the creation or annihilation of matrix phonons. However, this structure on spectral bands is often masked in practice by the inhomogeneous broadening. In particular, this takes place for impurity phthalocyanine molecules in an amorphous polyvinyl butyral matrix, as shown in Fig. 2. The shape of spectral bands observed in experiments depends on the strength of electron–phonon interaction and temperature.

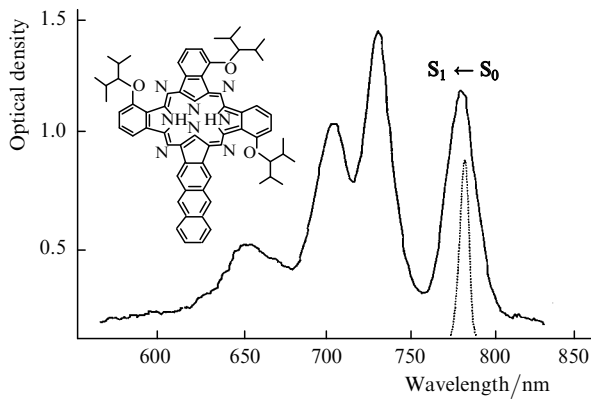


Figure 2. Low-temperature absorption spectrum of phthalocyanine molecules in a polyvinyl butyral film [4]. At the left is shown the structural formula of the phthalocyanine molecule. Laser excitation was performed into the $S_0 \rightarrow S_1$ absorption band.

The ratio of the ZPL and PSB intensities, their width and shape, and the ZPL position strongly depend on temperature. The ZPL intensity decreases with increasing temperature and the ZPL vanishes at room temperature. In this case, optical coherent responses can be excited only through PSBs [8]. For this reason, this excitation is theoretically described by using multilevel systems including (for example, in the case of phthalocyanine molecules) the electronic levels Ψ_{S_0} and Ψ_{S_1} and a set of vibronic levels Ψ_{q_i} from which the nearest vibronic level is taken in the simplest case, where q_i is the wave vector of a phonon involved in the electronic transition (see Fig. 3).

Because it was found experimentally [9, 10] that irreversible dephasing in such systems at high temperatures is caused by the interaction of impurity molecules with localised low-frequency vibrational modes (LFMs) and the constant of this interaction achieves 110 GHz already at 30 K [10], we will assume below that phthalocyanine molecules in the impurity polymer sample under study acquire the vibrational energy due to interaction with LFMs. Of course, the limiting constants of such interaction at room temperature can be an order of magnitude higher (taking into account the homogeneous width of the $S_0 \rightarrow S_1$ line equal to 5×10^{12} kHz [1, 2]). Because phthalocyanine is a polyatomic molecule (see Fig. 2), the number of its normal vibrations acquiring the energy from LFMs is large. This allows us to interpret the LFM reservoir as an efficient

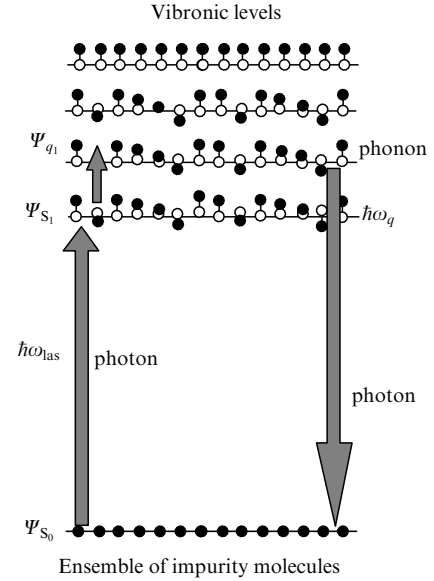


Figure 3. Energy level diagram in which anti-Stokes free induction decay and echo signals are formed: ω_{las} is the laser-pulse carrier frequency; ω_q is the phonon pulse frequency.

phonon quantum generator (or an acoustic wave generator) acting on a system of impurity molecules. Because a ‘lattice’ phonon has no time to lose its phase during the action of a femtosecond pulse, such a quantum generator can be called coherent.

Let us assume that the simultaneous action of the laser and acoustic pulses on a sample is equivalent to the action of an effective photon–phonon generator of coherent waves on impurity molecules. For simplicity we consider first the three-level system Ψ_{S_0} , Ψ_{S_1} , Ψ_{q_1} , where Ψ_{S_1} is the intermediate state in the two-photon transition. We assume that the pulse acts for a short time Δt , after which an impurity molecule begins to relax during the time $t \gg \Delta t$. The time evolution of the impurity molecule initiated by the photon–phonon pulse can be described in the second order of the perturbation theory by the interaction Hamiltonian

$$V_{mn}^{(2)} = \frac{1}{2} \sum_{n'} \frac{V_{mn}(\mathbf{k}_{\text{las}}) V_{n'n}(\mathbf{q})}{\omega_{\text{las}} - \omega_{n'n}} + \frac{V_{mn}(\mathbf{q}) V_{n'n}(\mathbf{k}_{\text{las}})}{\omega_q - \omega_{n'n}}, \quad (1)$$

where V_{mn} are the matrix elements of the interaction operator; m , n , and n' are the sets of states Ψ_{S_0} , Ψ_{q_1} , and Ψ_{S_1} , respectively; \mathbf{k}_{las} is the wave vector of the laser pulse; \mathbf{q} is the phonon wave vector; ω_{las} is the carrier frequency of the laser pulse; ω_q is the phonon pulse frequency. Thus, under conditions when the shape of each pulse is assumed rectangular and the duration of optical and acoustic pulses are the same, the interaction of each j th active impurity molecule with the radius vector \mathbf{r}_j can be described by the Hamiltonian

$$H_{\text{int}}^{\text{eff}} = -\frac{\hbar}{2} \left[\frac{\langle \Psi_{q_1} | \mathbf{p} \mathbf{E}_{0\text{las}} | \Psi_{S_1} \rangle \langle \Psi_{S_1} | H'_{\text{SPH}} | \Psi_{S_0} \rangle}{\omega_{\text{las}} - \omega_{S_0 S_1} + i\Delta\omega_{\text{inh}}} + \frac{\langle \Psi_{q_1} | H'_{\text{SPH}} | \Psi_{S_1} \rangle \langle \Psi_{S_1} | \mathbf{p} \mathbf{E}'_{0\text{las}} | \Psi_{S_0} \rangle}{\omega_q - \omega_{S_0 S_1} + i\Delta\omega_{\text{inh}}} \right] \times$$

$$\times [R_+^j e^{i(\mathbf{k}r_j - \omega t)} + R_-^j e^{-i(\mathbf{k}r_j - \omega t)}]. \quad (2)$$

Here, $\omega = \omega_{\text{las}} + \omega_q$; the frequency $\omega_{S_0S_1}$ corresponds to the $S_0 \rightarrow S_1$ transition; $\Delta\omega_{\text{inh}}$ is the inhomogeneous width of the $S_0 \rightarrow S_1$ line; $E_{0\text{las}}$ is the electric-field amplitude of the laser pulse; \mathbf{p} is the electric dipole; R_+^j and R_-^j are the raising and lowering operators of the atomic system; \mathbf{k} is the wave vector;

$$H'_{\text{SPh}} \approx \hbar\omega_{\text{LFM}} \left| \sum_{\alpha, \beta} F_{\alpha\beta\gamma\delta} d_{q,\gamma\delta} \right| \quad (3)$$

is the non-operator part of the spin–phonon interaction Hamiltonian [11]; $\hbar\omega_{\text{LFM}}$ is the energy of interaction of the active impurity molecule with the LFM reservoir (values of ω_{LFM} are presented, for example, in [10]); $F_{\alpha\beta\gamma\delta}$ is the tensor characterising the spatial position of nearest LFMs with respect to the directions of vibrational modes in the impurity molecule and the polarisation vector of the exciting laser pulse ($|F_{\alpha\beta\gamma\delta}| \leq 1$); $d_{q,\gamma\delta}$ is the tensor characterising the direction of polarisation of the q th vibrational mode with respect to molecular axes and the wave vector \mathbf{k}_{las} ($|d_{q,\gamma\delta}| \leq 1$).

By omitting the details of the calculation described in [12], we present the expression for the signal of free induction decay of the nonequilibrium electric polarisation (FIDEP) in the direction of the wave vector \mathbf{k} with the unit solid angle:

$$I_{\text{FIDEP}}(\mathbf{k}) = I_0(\mathbf{k}) \gamma^2 \sin^2 \theta \times \sum_i^N \sum_{j \neq i}^N \exp\{i[\mathbf{k} - (\mathbf{k}_{\text{las}} \pm \mathbf{q})](\mathbf{r}_i - \mathbf{r}_j)\}, \quad (4)$$

where $I_0(\mathbf{k})$ is the spontaneous emission intensity of a single impurity molecule in the anti-Stokes direction $\mathbf{k} = \mathbf{k}_{\text{las}} + \mathbf{q}$; $\gamma = \tanh(\hbar\omega_{\text{las}}/2k_{\text{B}}T)$; k_{B} is the Boltzmann constant; T is the sample temperature in kelvins;

$$\theta \approx \hbar^{-2} \Delta t \left[\frac{\langle \Psi_{q1} | \mathbf{p} E_{0\text{las}} | \Psi_{S_1} \rangle \langle \Psi_{S_1} | H'_{\text{SPh}} | \Psi_{S_0} \rangle}{\omega_{\text{las}} - \omega_{S_0S_1} + i\Delta\omega_{\text{inh}}} \right] \quad (5)$$

is the ‘area’ under a pulse of the effective generator. The second term in (5) is omitted because the phonon frequency is small compared to the laser pulse frequency ω_{las} . As a result, the pulse area can be estimated from the expression

$$\theta \approx \hbar^{-1} \Delta t p_{S_0S_1} E_0 \frac{\omega_{\text{LFM}}}{\Delta\omega_{\text{inh}}}, \quad (6)$$

where $p_{S_0S_1}$ is the modulus of the electric dipole moment of the $S_0 \rightarrow S_1$ transition; E_0 is the electric-field amplitude of a femtosecond laser pulse; ω_{LFM} is the frequency of the low-frequency mode. Let us estimate the value E_0 by using the known experimental data [1, 2]: the intensity I of a femtosecond laser pulse of duration $\Delta t = 6.5 \times 10^{-14}$ s and energy 600 mJ (i.e. 6000 erg) for the laser beam cross section $S = 3 \times 10^{-2}$ cm² is 3×10^{18} erg s⁻¹ cm⁻² (i.e. 3×10^{11} W cm⁻²). Then, $E_0 = (8\pi I/c)^{1/2} = 5 \times 10^4$ V cm⁻¹. By assuming that $p_{S_0S_1} \approx 10^{-20}$ CGSE units, $\omega_{\text{LFM}} \approx 10^{12}$ Hz, and $\Delta\omega_{\text{inh}} \approx 10^{13}$ Hz, we obtain $\theta \approx 10^{-3}$, and therefore $\sin \theta$ can be replaced by θ . Note that for the laser beam focal spot area $S = 10^{-7}$ cm² (as in [13]), we have the

intensity $I = 10^{24}$ erg cm⁻² s⁻¹ = 10^{17} W cm⁻², and the electric field strength is $E_0 \approx 3 \times 10^7$ V cm⁻¹. In this case, we obtain $\theta \approx 0.5 < 1$, i.e. we are still dealing with the regime of small pulse ‘areas’.

In expression (4), it is necessary to perform double summation over the number of active molecules, integration over solid angles, the scatter of local fields $\Delta\omega_j$ and the scatter of the wave vectors q_i of phonon modes. As a result, after the first three operations, the total FIDEP intensity can be estimated from expression

$$I_{\text{FIDEP}} = I_0 N^2 \gamma^2 \theta^2 \lambda^2 / 4\pi, \quad (7)$$

where λ is the FIDEP wavelength. The anti-Stoked component of this signal is emitted by a sample in the wave vector direction

$$\mathbf{k}_{\text{FIDEP}} = \mathbf{k}_{\text{las}} + \mathbf{q}_{\text{eff}}, \quad (8)$$

where \mathbf{q}_{eff} is the wave vector of the ‘effective’ phonon mode.

The intensity of an anti-Stokes femtosecond photon echo (AFPhE) can be calculated similarly. For this purpose, we collect our photon–phonon pulses in sets of pulse pairs acting successively on a resonance system. As a result, we obtain the expression

$$I_{\text{AFPhE}} = I_0 N^2 \gamma^2 \theta^6 \lambda^2 / 64\pi, \quad (9)$$

and the phase-matching condition will take the form

$$\mathbf{k}_{\text{AFPhE}} = 2(\mathbf{k}_{\text{las}1} + \mathbf{q}) - (\mathbf{k}_{\text{las}2} + \mathbf{q}), \quad (10)$$

where $\mathbf{k}_{\text{las}1}$ and $\mathbf{k}_{\text{las}2}$ are the wave vectors of the first and second femtosecond laser pulses in a pulse pair.

In experiments [1, 2], the phonon wave vector \mathbf{q} was not manifested under spatial phase-matching conditions for the AFPhE signal. The explanation of this fact requires a separate investigation and is beyond the scope of our study. In our opinion, this is related to the fact that a phonon is treated as a particle having the energy of a normal vibrational mode of the atomic system. However, in fact the vibrational energy is distributed in real space over the entire polymer matrix and is localised in the space of \mathbf{q} и ω_q . Therefore, one of the variants of the explanation is that, because impurity molecules in an amorphous matrix are distributed randomly, the phonon wave vector disappears from spatial phase-matching conditions after averaging over random directions of \mathbf{q} for different vibrational modes.

3. Coherent regime of laser cooling of doped polymer films

The first important condition for realisation of laser cooling is that a coolant of a real laser refrigerator should be at room temperature. Therefore, the results of all previous low-temperature echo experiments with solids could not be used for cooling. The second condition is the use of the femtosecond excitation regime, which creates the phase memory on the electron–phonon transitions in the impurity system and provides a high cooling rate, which is proportional to the square N^2 of the number of active molecules. The third condition is the use of dye molecules

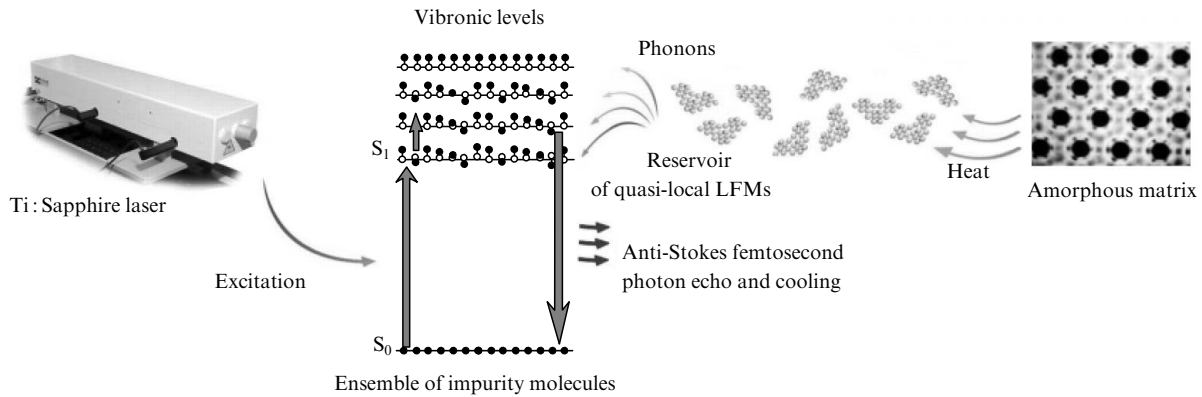


Figure 4. Scheme illustrating the regime of femtosecond coherent laser cooling.

as ‘working’ impurities, which have broad absorption bands that provide the efficient absorption of broadband femtosecond pulses.

The cooling of doped polymer films can be performed in the following way. Dye molecules are excited by femtosecond pulses not at the purely electronic $S_0 \rightarrow S_1$ transition but at the transition from the ground S_0 electronic state to the upper vibronic state, involving the laser photon and a ‘lattice’ phonon. As a result, each of the ‘working’ molecules is excited to the superposition state, in which it has the nonequilibrium pseudoelectric dipole moment and phase memory. An ensemble of impurity molecules in this state emits a coherent free-induction-decay signal, which carries away from the sample both the energy of the absorbed photon and phonon energy, thereby cooling the sample. We see that cooling is performed in the anti-Stokes regime. The subsequent irradiation of the same region by the second and third resonance femtosecond pulses causes the emission of the primary and stimulated femtosecond photon-echo signals, followed by the sample cooling. In the presence of the phase memory, these signals are formed due to reversible dephasing, which is directly related to the inhomogeneous line broadening.

There exists another important circumstance – irreversible dephasing, which determines the fourth condition required for the realisation of coherent cooling. The experimental studies performed for many years by Vainer and his colleagues [9, 10] have shown that irreversible dephasing in doped polymer films at high temperatures appears due to the existence of a virtually continuous band of quasi-local low-frequency vibrational modes in the range from 10 to 30 cm^{-1} at temperature 30 K (at room temperature these frequencies are considerably higher). The fourth condition of the optimal cooling is that the LFM band corresponds to the homogeneous linewidth obtained in femtosecond echo experiments ($\Gamma_{\text{hom}} = 5 \times 10^{12} \text{ s}^{-1}$ at room temperature [1]). It can be shown that such a correspondence takes place. On the other hand, the LFM band should be matched with the blue shift of the echo-signal spectrum. Under these conditions, the energy from the LFM reservoir continuously transfers to impurity molecules. Thus is illustrated in Fig. 4.

4. Conclusions

We have considered the physical principles of femtosecond coherent cooling. Situations related to the generation of

free-induction-decay signals and femtosecond echo signals have been considered. It has been proposed to verify the possibility of realising a new regime of laser cooling by performing the following descriptive experiment. First it is necessary to irradiate a sample by a femtosecond laser pulse or a pair of such pulses in the absence of resonance (for example, at a wavelength of 750 nm) and to see that the sample is heated and even its optical breakdown can occur. Then, the experiment should be repeated upon resonance excitation at 793 nm. One can expect that the sample temperature will increase and the conditions of its operation will be considerably improved. This can be verified with the help of a remote IR thermometer. Because the sample under study is promising as a data carrier of an optical echo processor, the realisation of the coherent optical cooling regime is of practical importance. In our opinion, the outlook for this cooling regime is related to multipulse laser trains of the WAHUA type [5, 6], which provide the simultaneous narrowing of the homogeneous linewidth.

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