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Optically-induced second-order nonlinear optical effect in polyvinyl alcohol photopolymers

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Abstract

IR induced picosecond nonlinear optical effects in polyvinyl alcohol photopolymer is investigated. The second harmonic generation (SHG) is studied versus the pump power and delaying time between the pump and probing beam ($\lambda = 1.55$ and 1.32 μm, respectively). The phenomena are explained within a framework of fifth-order nonlinear optical susceptibilities. An explanation of the observed dependences is given within a framework of photostimulated vibrations, which enhance acentric electron–phonon anharmonicity. Temperature dependences of the observed phenomena fully confirm the electron–phonon anharmonic origin of the observed effect.

Keywords: Optical properties of polymers; Polyvinyl alcohol polymers; Nonlinear optics

From general symmetry rules second-order optical effects including light second harmonic generation (SHG) are forbidden in randomly-disordered media, particularly in polymers [1]. To create an acentricity an external electric field is applied (for example electrically-induced SHG) [2]. In the case of photopolymers possessing relatively high ionic conductivity and bulk non-homogeneity the considered method is insufficient. Simultaneously the contribution of photoinduced anharmonic phonons in such kinds of systems may be crucial how it was just shown for the glasses [3,4].

The photo-stimulated treatment in polymers becomes increasingly attractive, since it may be used in optically operated waveguides for recording and transmission of optical information in the infrared spectral range. The PVA photopolymers [5] seem to be more promising because they possess good acousto and opto-mechanical properties, so the IR-induced vibrations could play here substantial role. However, physical insight of the IR-stimulated changes and the corresponding second-order nonlinear optical properties are principally different for the photopolymers compared to other disordered substances, particularly, for glasses. The principal difference consists in possibility of creation the additional IR-induced chemical bonds in PVA due to appearance of the IR-induced breaking bonds, particularly photo-initiated ones. So it should be substantial contribution of optically induced electron-vibration interactions (EVI) to the second-order nonlinear optical susceptibilities [6]. The anharmonic EVI are described by third-order space derivatives of the electrostatic potential similarly the second-order susceptibilities. As a consequence from general group theory analysis, the second-order optical effects might be enhanced. However, following the general phenomenological consideration one can expect a necessity to introduce the nonlinear optical susceptibilities of higher orders.

In this paper is proposed a new type of optical treatment consisting in photo-pumping of appropriate vibrations.

The main goal of the present work is to explore how pump–probe, nonlinear optics of the photopolymer may

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be applied to investigate EVI and dynamics of the IR pump light in the PVA. In the present paper are given novel nonlinear optical effects associated with the IR photoinduced anharmonic lattice–electron interactions. As a consequence one can expect an appearance of optically induced electron–phonon anharmonic non-centrosymmetry in electronic charge density distribution of particular PVA structural chains.

In the case of the optical poling the IR-induced non-centrosymmetry of the photoexcited vibrations begins to play dominant role and it is necessary to consider a process of interaction of at least two photons and three phonons or a fifth-order process. Interactions with one or two phonons could not give a contribution to the non-zero polarization of the medium (see Fig. 1(a) and (b)). So for explanation of the observed phenomenon only anharmonic electron–phonon interactions with at least three phonons should be considered (see Fig. 1(c)).

Because the non-centrosymmetric photoinduced electron–phonon anharmonicity requires participation of at least three phonons (otherwise we would have a harmonic electron–phonon (see Fig. 1(b)) interactions which would not give the non-centrosymmetry), the SHG effect should be described by an equation:

$$P_i = d_{ijklmn} \cdot E_j^{(\omega)} \cdot E_k^{(\omega)} \cdot \Omega_l(1) \cdot \Omega_m(2) \cdot \Omega_n(3), \quad (1)$$

where d_{ijklm} is fifth-order NLO susceptibility; $\Omega_l(1)$, $\Omega_m(2)$ and $\Omega_n(3)$ are the interacting phonon's displace vectors (induced by pump light) participating in the photoinduced anharmonic EPI process; $E_{kj}^{(\omega)}$ pump beams with polarization k, j, respectively. This process is substantially different compared to usual harmonic interactions because due to specific symmetry of the process the total polarization in the last case will give zero [7,8]. Microscopic calculations performed by a method similar to the described in the Ref. [9] have

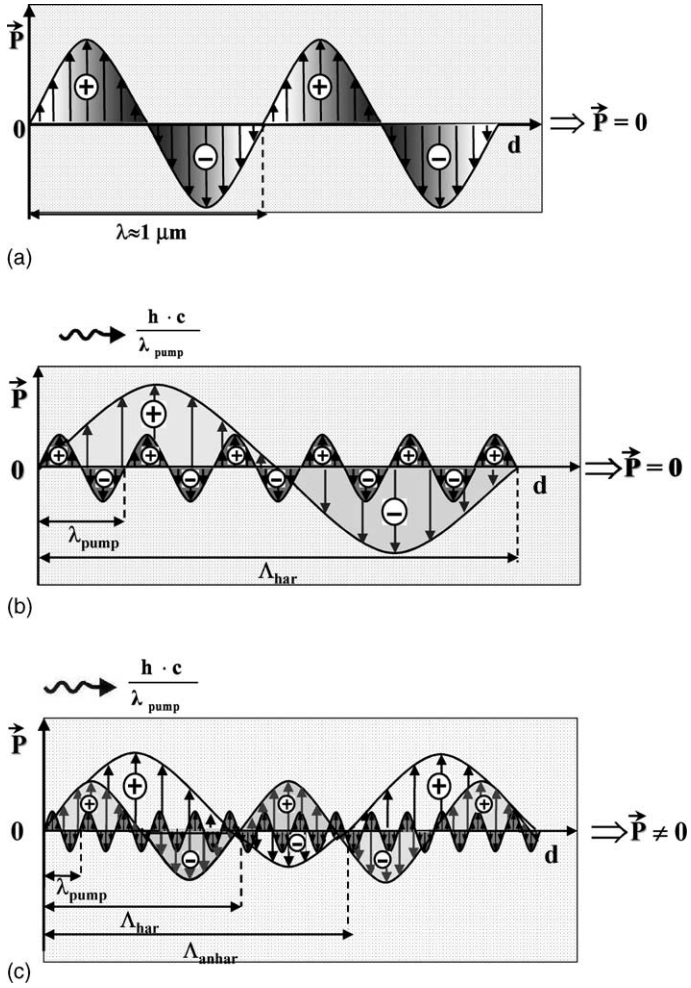

Fig. 1. (a) General scheme of the medium polarization for the pure electronic contribution, (b) electronic + harmonic electron–phonon contribution and (c) electronic + harmonic electron–phonon + anharmonic electron–phonon contributions.

shown that optically-induced charge density non-centrosymmetry is caused by anharmonic EVI. The performed calculations have shown that the PVA photopolymer chains play a dominant role in the experimentally-observed IR-induced optical susceptibilities d_2. For the inter-cluster bonds the IR-induced changes are relatively low (less than 0.25%). For example the matrix dipole moments in the case of PVA photopolymer backbone are equal to about 12.6 Debye (D) calculated by semi-empirical AM1 method. For comparison the inter-chain total dipole moments are equal to about 0.25 D. The process of interaction of the probing Nd-YAG laser beam with the investigated medium may be also described as non-coherent interaction of the pumping and probing laser beams.

Appearance of a term with frequency 2ω is caused by photoinduced charge density non-centrosymmetry and is similar to the process of interference between the two coherent waves with the fundamental and doubled frequencies. The temporally averaged output nonlinear polarization for the doubled frequency may be associated with interaction of electromagnetic wave with non-centrosymmetric media created due to anharmonic electron–phonon interaction. More detailed theory is presented in the Ref. [9].

We can consider all the process as a scattering of the probing wavelength on the non-centrosymmetry grating created due to electron–phonon anharmonic interaction described by third-order polar tensor.

The amplitudes of the photoinduced anharmonic modes should be proportional to the pumping photoinduced IR power. From general phenomenological consideration of the PVA structure one can conclude that maximal output SHG should be achieved for parallel polarizations of IR-inducing and probing beams. This one reflects a fact that direction of the photoinduced charge density shift should be always parallel to the pumping polarization. The effect of second-order optical effect's appearance may be observed because there exist a range of phonon frequencies satisfying conditions: $\omega - \omega_1 \pm \Omega_1 \pm \Omega_2 \pm \Omega_3 = 0$ which are necessary for appearance non-centrosymmetric tensor components during the picosecond photoexcitation.

Taking into account the nonlinear interactions between fundamental (probe) wave with wave vector doubled frequency wave, pump wave with the frequency as well as the photoinduced combined anharmonic frequencies with the wave vectors, one can obtain a wide spectrum of angles satisfying phase matching conditions:

The range of angles satisfying phase matching conditions will be in this case relatively large because there exist large groups of electro-stricted vibrations (due to specific elastic properties of the PVA polymers) satisfying phase matching conditions within the spectral range 0.5–1 μm.

The theoretically evaluated dependences of the SHG using an approach presented in the Ref. [9] of the SHG versus the photoinducing power I and temperature T are depicted in the Fig. 2. The performed calculations predict an enhancement of the IR-induced SHG with an increasing pump power. However more surprising seems to be an appearance of the local minimum for the SHG at temperatures about 210 K, corresponding to the inclusion of EVI interactions.

The SHG was evaluated using experimental Maker fringes method [10]. The equipment (see Fig. 3) allows to carry out the measurements of the output SHG using as a fundamental the Nd^{3+}-YAG laser ($\lambda = 1320$ μm; $P = 18$ MW; $\tau = 0.44$–80 ps, frequency repetition 8–15 Hz) serving as a probing light. As a pumping Q-switched YAB-Eu laser ($\lambda = 1530$ μm; P = 27 MW; $\tau = 0.34$–90 ps, frequency repetition 10 Hz) was applied.

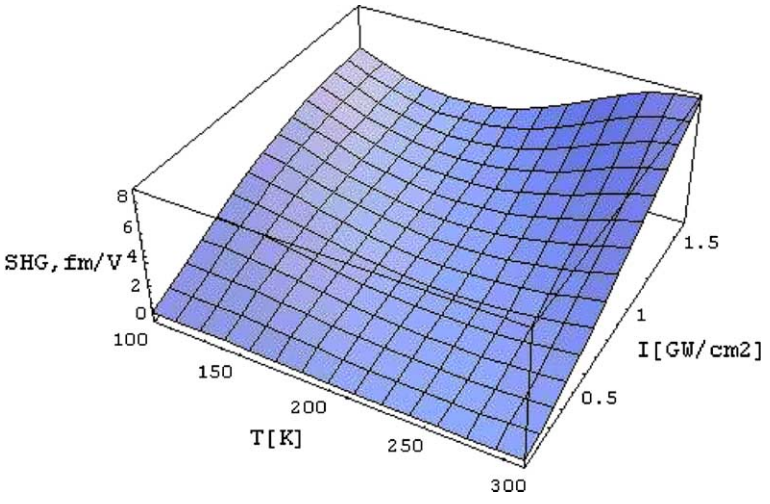

Fig. 2. Theoretically calculated dependence of photoinduced SHG versus photoinducing CO-laser power (I) and temperature (T).

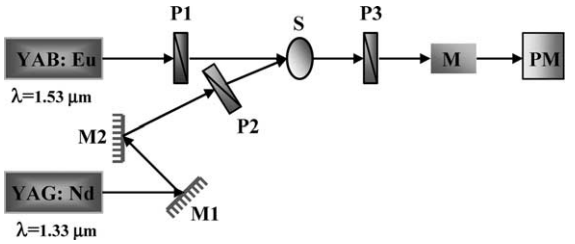

Fig. 3. General set-up of the IR-induced measurements. M1 and M2 are mirrors; P1, P2 and P3 are polarizers; M—grating IR monochromator; PM—photomultiplier.

Fast response photomultiplier, which is connected with an electronic boxcar integrator (gain time up to 530 ps), was used for detection of the output SHG signal. The laser beam was moved through the surface to average sample's surface non-homogeneity with varying incident angles within −28° to 28°. The Maker fringe pattern demonstrated a good symmetry and the SHG output signal achieved a maximum at angles lying within the 19–24°. The output SHG was varied within the 10^{-6}–10^{-7} compared to the incident beam (signal). Calculations of the SHG tensor values were done taking into account Fresnel losses, Gaussian-like profile of the beam, optical attenuation as well as appearance the photoinduced birefringence (10^{-1}–10^{-2}). The performed calculations showed that the maximal output SHG exists for parallel polarization of pumping and probing laser beams. Angle between these beams should not exceed 2.5°. Fluorescence signal was appeared for spectral wavelengths about 0.38 μm and was spectrally slightly separated by grating monochromator with spectral resolution 7 nm/mm. The time duration of the SHG signal was equal about 3 ps. The measurements of the photoinduced birefringence to correct the phase matching conditions was done using a Senarmont schema. The precision of the second-order optical's coefficient determination was about 6 fm/V.

In the Fig. 4 are presented the measured dependencies of the SHG ($\chi^{(2\omega)}$) at different pump laser powers ($\lambda = 1.55$ μm). An increase of the photoinduced SHG with increase of the pumping power densities within 0–1.8 GW/cm^2 is observed. With increasing temperature, the values of the photoinduced SHG increases achieving relatively large value (about 5.0 fm/V). Temperature behavior is in a good agreement with the theoretically calculated (see Fig. 2). The maximal values of the SHG signal is limited by IR destruction of the samples.

All experimental values obtained for SHG converge to about 5.0 fm/V when the intensity tends to 1.86 GW/cm^2. The diagonal tensor component $\chi^{(2\omega)}_{xxxxx}$ values are larger than all off-diagonal tensor component of about one order. For the pumping powers higher than 1.90 GW/cm^2 photochemical destruction begin to play a main role. From the Fig. 4 one can see that with

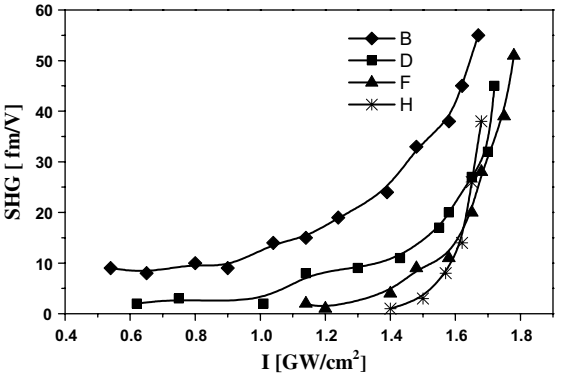

Fig. 4. Pump dependence of the SHG susceptibility (in $\times 10^{-1}$) at different temperature: H—150 K; F—77 K; D—210 K; B—300 K.

increasing temperature up to 300 K the value of the PISHG increases also.

A good agreement between theoretical curves and experimental results is observed. One can see an appearance of the minimum in the PISHG at temperature about 150 K in accordance with the theoretical predictions (see theoretically calculated SHG in the Fig. 2). This one reflects inclusion of photoinduced anharmonic electron-vibration interactions.

From the Fig. 5 one can see that the maximal SHG signal was observed for the pump–probe delaying times about 42 ps at room temperature. Only appropriate inclusion of the anharmonic EPI interactions described by the fifth-order tensor can explain the observed dependence.

To confirm theoretical expectation concerning a dominant role played by EVI, the changes of the IR

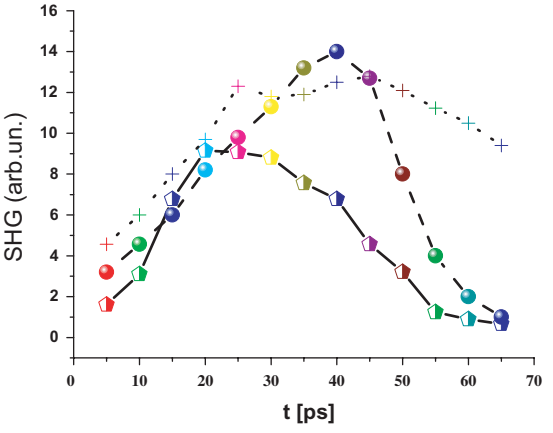

Fig. 5. Typical time-delayed dependences of the PISHG at pump power 1.3 GW/cm^2. At different temperature: (+) experimentally measured; (●) theoretically calculated with inclusion of the anharmonic EVI and without the inclusion of the EVI (⬠).

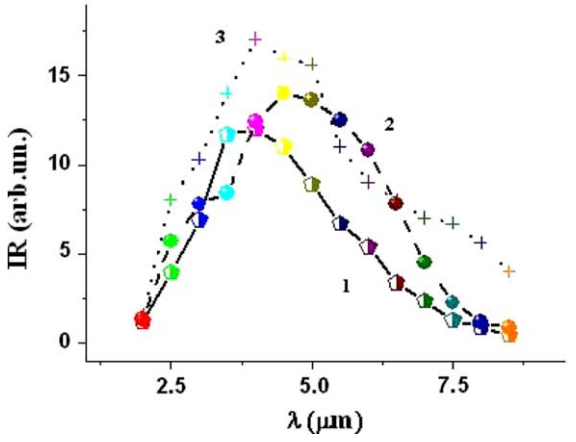

Fig. 6. Dependence of the IR-induced anharmonic phonon vibration modes at different pump power densities: 1–1 GW/cm^2; 2–1.2 GW/cm^2; 3–1.5 GW/cm^2.

absorption spectra within the 4–7 μm were measured under influence of laser pumping beams at $T = 300$ K (see Fig. 6). It was shown that increasing photoinducing beam power densities favor appearance of additional IR modes within the spectral ranges 3–7 μm. Such increase correlates well with the observed second-order optical effects and may be serve as a direct confirmation of the substantial contribution the EPI to the output nonlinear optical susceptibilities performed theoretically (see Fig. 1).

Conclusions

In summary, the macroscopic IR induced charge density noncentrosymmety phenomenologically described by the fifth-order nonlinear optical susceptibility is predicted and experimentally discovered in the PVA photopolymers for the first time. Substantial contributions of anharmonic electron-vibration subsystem induced by pumping IR-laser is shown. Using quantum chemical methods the fifth-order nonlinear optical origin of the observed phenomenon is demonstrated. Independent measurements of the photoinduced spectra directly indicate good correlation between the number of the photoexcited IR modes and the observed SHG. The pump–probe time evolution of the observed effect is consistent with a simple model of electron–phonon anharmonic interactions.

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