Eur. Phys. J. D **20**, 129–131 (2002)
DOI: 10.1140/epjd/e2002-00102-7

THE EUROPEAN PHYSICAL JOURNAL D

Third harmonic generation of laser radiation in Fe- and Zn-doped polyvinylpyrrolidone

R.A. Ganeev[1,a], A.I. Ryasnyansky[2], M.K. Kodirov[2], S.R. Kamalov[1], V.A. Li[3], R.I. Tugushev[1], and T. Usmanov[1]

[1] NPO Akadempribor, Akademgorodok, Tashkent 700143, Uzbekistan
[2] Samarkand State University, Samarkand 703004, Uzbekistan
[3] Institute of Chemistry and Physics of Polymers, Tashkent 700128, Uzbekistan

Received 30 November 2001 / Received in final form 27 March 2002
Published online 28 June 2002 –

Abstract. The results of third-order nonlinear susceptibilities studies of Fe- and Zn-doped polyvinylpyrrolidone (PVP) aqueous solution in processes of third harmonic generation of Nd:YAG laser radiation are presented. Nonlinear susceptibilities of PVP:Fe and PVP:Zn were calculated to be 5×10^{-13} esu and 3×10^{-13} esu respectively. Third harmonic conversion efficiencies in these metallocomplexes were measured to be 8×10^{-7} and 5×10^{-7} respectively. The Z-scan method was applied to determine Kerr effect influence on frequency conversion process. The value of nonlinear refractive index of PVP:Fe at the wavelength of $\lambda = 1\,064$ nm was measured to be $n_2 = -6.7 \times 10^{-13}$ esu.

PACS. 42.65.Ky Harmonic generation, frequency conversion – 42.65.An Optical susceptibility, hyperpolarizability – 78.20.Ci Optical constants (including refractive index, complex dielectric constant, absorption, reflection and transmission coefficients, emissivity)

The investigations of optical and nonlinear-optical properties of organic compounds possessing double conjugated bonds in the processes of harmonic generation, optical limiting, optical switching, etc., are of great interest during last time. Such type of compounds covers a number of arenes (naphthalene, antrathene etc.), fullerenes, polymers, etc. π-electrons delocalization in such kind of organic molecules with double conjugated bonds is responsible for their high nonlinearities. For example, delocalized π-electrons in arenes cause the high values of transition dipole moments [1] and also responsible for high values of fullerenes' nonlinear susceptibilities, observed both at harmonic generation [2–4] and wave conjugation [5] processes. Metal injection into the polymer structure leads to the variations of their both optical and nonlinear-optical characteristics [6]. Note an interest on metal-doped polymers with conjugated stabilizers (in particular, polyphenylenevinylene and polyvinylpyrrolidone [7]). Polyvinylpyrrolidone (PVP) has an advantage of accepting of high concentrations of various guest molecules and atoms without the loss of its good optical properties (in particular the negligible scattering). PVP can be used as a stabilizer for nanostructures such as metal clusters that makes such polymer also interesting for the stable suspensions preparation for nonlinear-optical investigations [8,9].

Below we present our studies on nonlinear-optical parameters of PVP solutions doped with iron and zinc using third harmonic generation (THG) of picosecond Nd:YAG laser radiation. Nonlinear susceptibilities ($\chi^{(3)}(-3\omega,\omega,\omega,\omega)$), nonlinear refractive indices (n_2) and conversion efficiencies (η) of THG in these media were determined and the influence of Kerr nonlinearities on THG conversion efficiency was discussed.

Output characteristics of Nd:YAG laser radiation were as follows: pulse duration 35 ps, pulse energy 1 mJ, $\lambda = 1\,064$ nm. Laser radiation was focused by 25-cm focal length lens into the quartz cells with metallopolymer solutions. Pump radiation was registered by a calibrated photodiode. Converted radiation ($\lambda = 354.7$ nm) was filtered by UV filter from pump radiation and was directed to the spectrograph (DFS-452, LOMO) and registered by a photomultiplier tube (FEU-106, VNIIOFI). The laser radiation was converted to second and third harmonics in KDP crystals and the calibration of registrar apparatus was made for determination of the absolute values of conversion efficiencies.

The aqueous PVP solutions doped with iron (4.25 wt.%) and zinc (0.85 wt.%) were used. 1 g of metallopolymers was dissolved in 100 ml of distilled water at a room temperature. Investigated solutions were kept in 1-mm (in the case of Z-scan experiments) and 2-mm (in the case of THG experiments) cells. Our interest in application of PVP as a matrix were due to its stabilizing properties. Our nanoparticles had a longer life-time in respect to colloidal aqueous solutions which fall in the sediments after some period of aggregation.

[a] e-mail: rganeev@mail.tps.uz

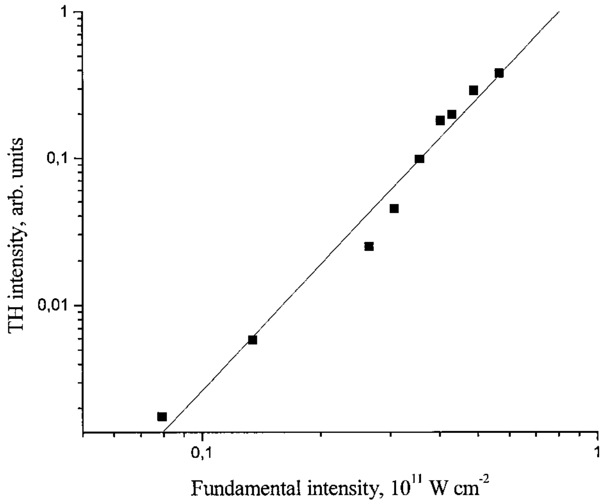

Fig. 1. The dependence of TH intensity *versus* pump radiation intensity for PVP:Fe solution.

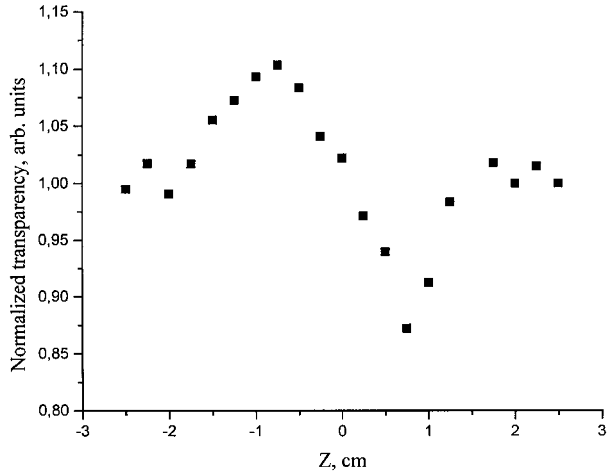

Fig. 2. Normalized transmittance as a function of sample's (PVP:Fe) position with respect to the focusing point ($Z = 0$) in closed aperture Z-scan scheme.

Figure 1 shows the dependence of third harmonic (TH) intensity on pump radiation intensity in the case of iron-doped PVP solution (PVP:Fe). The slope of $I_{3\omega}(I_\omega)$ dependence was 2.85 that was close to the theoretical predictions and remained approximately constant in the whole intensity range. The same features were in the case of zinc-doped PVP solution (PVP:Zn). The experiments took place at the intensities below the breakdown threshold of solutions ($I_{\rm thr} = 10^{11}$ W cm^{-2}). The maximal values of conversion efficiencies for PVP:Fe and PVP:Zn were measured to be 8×10^{-7} and 5×10^{-7} respectively. No THG was observed in pure PVP and other metal-doped PVP solutions, particularly in PVP doped with cobalt and manganese. Thus the role of π-bonds in PVP was negligible in respect to the influence of metallic nanoparticles on the nonlinear-optical properties of metal-doped PVP structures. The possible explanation of the fact that cobalt- and manganese-doped PVP solutions does not exhibit THG is that their surface plasmon resonances are situated far from two- or three-photon resonances with pump radiation frequency (in respect to iron and zinc nanoparticles).

One of the main factors which govern the conversion efficiency of laser radiation frequency in isotropic media is the self-interaction associated with a change of refractive index of medium in an electromagnetic field [10]. This effect alters the phase conditions of a nonlinear interaction between the waves and also results in a redistribution of the intensity of confined wave beams. The influence of the self-interaction has been analyzed previously by numerical and analytic methods. As a rule, an analysis has been made without full account for variation of the field along a transverse coordinate in a nonlinear medium [11,12].

The analysis of harmonic generation was used to determine the nonlinear susceptibilities responsible for harmonic generation. Analysis was first provided by a method taking into account the self-action effects caused by the Kerr nonlinearities [13]. In the case of weak focusing of fundamental radiation (medium length L much less than confocal parameter of fundamental beam b), there is following simple equation for third harmonic intensity taking into account the variations of the fields along a transverse coordinate (r) in a nonlinear medium:

$$I_{3\omega} = \gamma^2 L^2 I_{10}^3 \exp(-6k_1 r^2/b) \frac{\sin^2 \Delta(L,r)}{\Delta^2(L,r)}\,. \qquad (1)$$

Here $\gamma = 24\pi^3\chi^{(3)}(-3\omega,\omega,\omega,\omega)/(n_1^{3/2}n_3^{1/2}c\lambda_1)$; $\Delta(L,r) = 2b/L + \alpha - \beta$; $\alpha = L\Delta k$ is the normalized phase-mismatching; $\Delta k = k_1 - 3k_3$, $\beta = 72\pi^3 L\Delta\chi_k I_{10}\exp(-2k_1r^2/b)/(n_1^2 c\lambda_1)$; $\Delta_{\chi_k} = \chi^{(3)}(-\omega,\omega,-\omega,\omega)/2 - n_1\chi^{(3)}(-3\omega,3\omega,\omega,-\omega)/n_3$ is the difference of Kerr nonlinearities, responsible for refractive indices changes at the wavelengths of fundamental and harmonic radiation caused by fundamental radiation; λ_i, k_i and n_i are the wavelengths, the wave numbers and the refractive indices at the frequency of i-radiation, I_{10} is the maximal intensity at the plane of beam waist.

We estimated the influence of self-action effects caused by Kerr nonlinearities on phase characteristics of THG process in these media. The standard Z-scan method [14] was applied in order to determine the value and the sign of nonlinear refractive index of solutions. Figure 2 presents the dependence of normalized transmission as a function of PVP:Fe position respectively to the focal point in the case of closed aperture scheme at the wavelength of 1 064 nm. As one can see, the investigated solution demonstrates self-defocusing of laser radiation. In this case, the observed nonlinear process was due to the Kerr nonlinearities' influence. We neglect the influence of thermal lens on the process of self-defocusing. The studies of nonlinear absorption in open aperture scheme showed an absence of this process at investigated wavelength.

The value of nonlinear refractive index of PVP:Fe at the wavelength of $\lambda = 1\,064$ nm was measured to be $n_2 = -6.7 \times 10^{-13}$ esu. n_2 of pure PVP was of the order of 10^{-14} esu. Following to the theoretical calculations, this nonlinear variation of refractive index does not influences on $I_{3\omega}(I_\omega)$ dependence at the intensities used. The same conclusion was made in our previous THG investigation in colloidal platinum and copper [4]. Note that the deviation from the cubic dependence observed in fullerene-doped polyimide films [1] was due to considerable nonlinear variations of the refractive index. The same deviation was observed previously in gaseous media [15,16] when the high-frequency Kerr effect led to the phase-mismatching. The reverse case takes place in the media with positive sigh of n_2 when the phase parameter $\sin^2(\Delta kL/2)/(\Delta kL/2)^2$ increases with the growth of pump intensity. This peculiarity can be used for THG optimization in the media with normal dispersion [16].

The $\Delta k = k_3 - 3k_1 = 0$ conditions should be fulfilled to achieve the phase matching of THG in the case of plane waves interaction. The confocal parameter of radiation focused by a 25-cm focal length lens was 20 mm whereas the length of nonlinear medium was 2 mm, *i.e.* the conversion process took place in plane waves conditions. It is well-known that above-mentioned phase-matching conditions ($\Delta k = 0$) take place when the frequency of generated harmonic is located in the range of anomalous dispersion of medium [17]. The investigated solutions posses the normal dispersion in the range of $\lambda = 354.7$ nm, so the phase-matching conditions were not fulfilled for observed process. The value of nonlinear susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ in this case was estimated from relation [13] taking into account a negligible influence of Kerr nonlinearities:

$$\left|\chi^{(3)}\left(-3\omega,\omega,\omega,\omega\right)\right|^2 = \frac{\lambda_1^2 n_3 n_1^3 c^2 \eta}{256\sqrt{3}(\ln^3 2)\pi^5 L^2 I_\omega^2} \times \left(\frac{\sin(\Delta kL/2)}{\Delta kL/2}\right)^{-2}, \quad (2)$$

where I_ω is the pump radiation intensity, η is the conversion efficiency, c is the light velocity. Third-order nonlinear susceptibilities responsible for the harmonic generation in PVP:Fe and PVP:Zn determined from equation (2) were calculated to be 5×10^{-13} esu and 3×10^{-13} esu respectively.

Our previous studies of nonlinear-optical characteristics of colloidal metals [18] and fullerenes [4,19] and their exhibition of THG have shown that the concentration of active particles in solutions (Pt and Cu nanoclusters in aqueous solutions, C_{60} and C_{70} in toluene) seems to be crucial factor of frequency conversion efficiency. The concentration of nanoparticles should be chosen in appropriate manner for the optimization of conversion processes, so that the linear absorption at fundamental and harmonic frequencies and another limiting factors (nonlinear refraction, nonlinear absorption, etc.) did not prevented the growth of the conversion efficiency.

In conclusion, we investigated the nonlinear-optical characteristics of aqueous solutions of iron- and zinc-doped PVP. Third-order nonlinear susceptibilities responsible for third harmonic generation as well as TH conversion efficiencies were measured. The influence of high-frequency Kerr nonlinearities in PVP:Fe was negligible on the $I_{3\omega}(I_\omega)$ dependence.

R.A.G., S.R.K., R.I.T. and T.U. acknowledge the partial support of the Scientific and Technology Center in Ukraine under agreement UZB-29.

References

1. R.A. Ganeev, S.R. Kamalov, M.K. Kodirov, A.I. Ryasnyansky, T. Usmanov, Opt. Commun. **184**, 305 (2000)
2. J.S. Meth, H. Vanherzeele, Y. Wang, Chem. Phys. Lett. **197**, 26 (1992)
3. D. Neher, G.I. Stegeman, F.A. Tinker, Opt. Lett. **17**, 1491 (1992)
4. R.A. Ganeev, A.I. Ryasnyansky, N.V. Kamanina, M.K. Kodirov, T. Usmanov, J. Opt. B **3**, 88 (2001)
5. R.J. Knize, J.P. Partanen, Phys. Rev. Lett. **68**, 2704 (1992)
6. G.S. Pan, R. Kesavamoorthy, S.A. Asher, J. Am. Chem. Soc. **120**, 6525 (1998)
7. A. Samos, M. Samos, M. Luther-Davies, Proc. SPIE **3147**, 166 (1997)
8. Y.-P. Sun, J.E. Riggs, H.W. Rollins, J. Phys. Chem. B **103**, 77 (1999)
9. R.A. Ganeev, A.I. Ryasnyansky, M.K. Kodirov, S.R. Kamalov, V.A. Li, R.I. Tugushev, T. Usmanov, Appl. Phys. B **75**, 47 (2002)
10. V.G. Arkhipkin, A.K. Popov, *Nonlinear conversion of light in gases* (Nauka, Novosibirsk, 1987)
11. R. Mahon, M.Y. Yun, Opt. Lett. **5**, 279 (1980)
12. D.M. Mittleman, D.C. Douglass, Z. Henis, J. Opt. Soc. Am. **13**, 170 (1996)
13. I.A. Kulagin, T. Usmanov, Quant. Electron. **28**, 1092 (1998)
14. M. Sheik-Bahae, A.A. Said, T. Wei, D.J. Hagan, E.W. van Stryland, IEEE J. Quant. Electron. **26**, 760 (1990)
15. L.J. Zych, J.F. Young, IEEE J. Quant. Electron. **14**, 147 (1978)
16. R.A. Ganeev, I.A. Kulagin, I.A. Begishev, V.I. Redkorechev, T. Usmanov, Nonlin. Opt. **16**, 109 (1996)
17. J.F. Reintjes, *Nonlinear optical parametric processes in liquids and gases* (Academic Press, London, 1984)
18. R.A. Ganeev, A.I. Ryasnyansky, M.K. Kodirov, S.R. Kamalov, T. Usmanov, J. Phys. D **34**, 1602 (2001)
19. R.A. Ganeev, A.I. Ryasnyansky, M.K. Kodirov, T. Usmanov, Opt. Commun. **185**, 473 (2000)