

Photoinduced piezoelectric and elastic effects in the 2-cyclooctylamino-5-nitropyridine–C₇₀ complexes

NATALIA V. KAMANINA¹, JAN OWSIK^{2*}, BEATA RUSEK³

¹Vavilov State Optical Institute, 12 Birzhevaya Line St., St.-Petersburg 199034, Russia

²Military University of Technology, 2 Kaliskiego St., 00-908 Warsaw, Poland

³WELDI S.C., 1 Pszczyńska St., 43-175 Wry, Poland

*Corresponding author: owsik1957@wp.pl; jowslk@wat.edu.pl

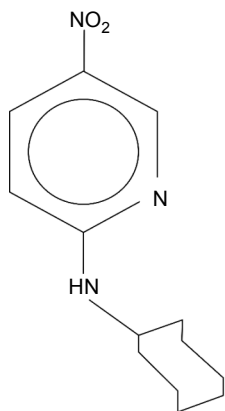
We have observed the piezoelectric and elasto-optic effects for the 2-cyclooctylamino-5-nitropyridine complex, chromophore doped by an inter-molecular acceptor – fullerene C₇₀. The discovered features may be used for optically operated piezoelectric triggers, modulators and deflectors. The observed effects are caused by the effective interaction of external light with the polarizable chromophore. As a pumping laser beam we have used both a nanosecond fundamental 1064 nm laser wavelength as well as its second harmonic generation at 532 nm. A principal role in the observed effects play photoinduced anharmonic phonons, effectively contributing to the output effect.

Keywords: nonlinear media, piezooptical effect, 2-cyclooctylamino-5-nitropyridine (COANP), fullerene, interaction mechanisms.

1. Introduction

Recent developments in laser technique and optically operated piezoelectric sources favor an interest in extensive research and designing of new nonlinear optical, piezooptical and piezoelectric materials possessing embedded effective nanochromophores. The latter are especially important for production of laser operated devices like triggers, modulators, memory and deflector devices [1–7]. These technical requirements stimulated an effective search for optical materials, with properties which can effectively change their optical and piezooptical coefficients. Among these materials, the systems based on 2-cyclooctylamino-5-nitropyridine (COANP) (see Fig. 1) play a unique role due to their highly charge transferred delocalized π -conjugated electron states. It is necessary to emphasize that such chromophores have just been partially studied, what was reported in Refs. [8–13].

COANP chromophore is a promising molecule with an effective intra-molecular charge transfer process between the NH– (donor) and NO₂– (acceptor). This intra-molec-



◀ Fig. 1. COANP molecule.

ular charge transfer can be modified using molecular materials engineering. Their electron affinity energies for intra-molecular acceptor fragments of COANP are varied between 0.4–0.54 eV. For example, the electron affinity energy of C_{60} and C_{70} is equal to about 2.65 eV. Thus, the inter-molecular acceptor fragment electron affinity energy is at least five times higher. Therefore, embedded chromophores are stronger sensitizers and they determine the acceptor fragments of an intra-molecular molecule. In this case, the intra-molecular electrostatic field gradient leads to an enhanced ground state dipole moment. So the increase in local volume polarizability stimulates the increase in dipole polarizability as well as the increase in charge carrier mobility.

In this paper we present the studies of laser induced piezoelectricity and piezooptics of the COANP system (see Fig. 1) doped with fullerene C_{70} . It may be recommended for use as a promising material for photoinduced acoustooptical modulators operated by external light.

2. Experiment

In our experiments, the fullerene-doped COANP films possessing thickness equal to about 3–4 μm thick were prepared by spin-coating of the solution in 1,1,2,2-tetrachloroethane on a glass substrate. A small amount of non-photosensitive polyimide structure has been used as a plasticizer in order to form the homogenous solid film. The fullerene concentration was varied within 0.5–5 wt%. Absorption spectra of the investigated systems were measured by a Perkin Elmer Lambda 9 spectrometer in the 200–3000 nm region with spectral resolution of about 0.5 nm.

The photoinduced piezoelectric and elastic changes were excited by Nd:YAG laser operating at 1064 nm in 15 ns regime with frequency repetition up to 1.2 kHz. The pulse energy of the 1064 nm photoinducing laser was varied within the 40–70 mJ and the pulse energy of the frequency doubled using BiB_3O_6 single crystal was equal to 20–30 mJ. Its diameter was fixed at 3–4 mm and the Gaussian-like contour was

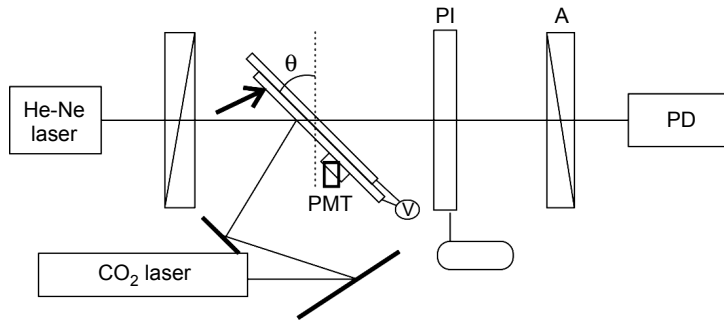


Fig. 2. Measurement set-up for photoinduced piezoelectrics and piezooptics. PMT – piezomodulated transducer, PD – photodetector.

used. The incident angle of the photoinducing laser beam was varied within $22\text{--}24^\circ$ to achieve the maximal output response.

The probing of the piezooptical effect was measured by a cw He-Ne laser with the powered density 3 mW, to exclude any overheating. The traditional Senarmont method used for analogous studies of other polymer composites was applied (see Fig. 2). Usually the mechanical field was applied by an external piezoelectric transducer which formed the mechanical field at a frequency of about 1 MHz. The same field was used for the measurement of the piezoelectric coefficient. The set-up allows for registration of the changes in the birefringence with a precision up to 10^{-6} and of the piezoelectric coefficient with a precision up to 0.1 pm/V. The method is partially similar to Ref. [8].

The laser treatment was done simultaneously with the $1\ \mu\text{s}$ CO₂ laser treatment. The observed effect achieved its maximum after 4–6 min of the photoinduced treatment and was controlled by the saturation of a CO₂ laser beam.

3. Results and discussion

Absorption spectra of the system studied are shown in Fig. 3. The absorption spectrum of COANP–polyimide–fullerene composite shows substantially different spectral features than the spectra of COANP–polyimide or polyimide–C₇₀ systems. There are two additional absorption peaks – at 490 nm and 810–820 nm. In the present paper we explain these peculiarities with inter-molecular charge transfer features and support them via analytic calculations, mass-spectrometry and nonlinear optical experiments [11–13]. It should be emphasized that for all investigated COANP systems, the nonlinear characteristics lie within the range: $n_2 = 10^{-10}\text{--}10^{-9}\ \text{cm}^2\text{W}^{-1}$ and $\chi^{(3)} = 10^{-10}\text{--}10^{-9}\ \text{cm}^3\text{erg}^{-1}$. In comparison, for quartz, which is a classical material traditionally used for nonlinear optics, the values of n_2 and $\chi^{(3)}$ are $(2.5\text{--}3)\times 10^{-16}\ \text{cm}^2\text{W}^{-1}$ and $10^{-14}\ \text{cm}^3\text{erg}^{-1}$ (esu), respectively. Thus, the systems studied reveal increased nonlinear optical parameters via photorefractive estimation.

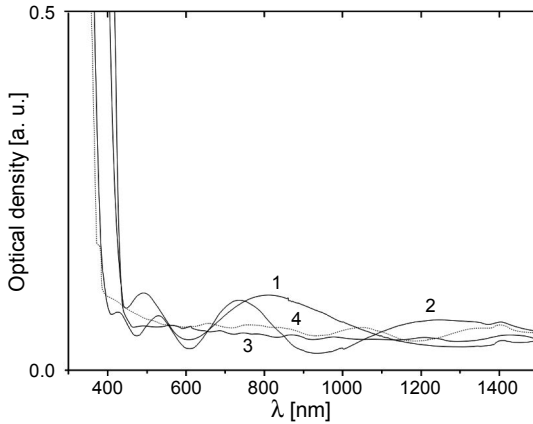


Fig. 3. Absorption spectra: 1 – fullerene-doped COANP–polyimide structure, 2 – pure polyimide, 3 – C_{70} -doped polyimide, and 4 – fullerene-free COANP–polyimide.

The photoinduced piezoelectrics for the d_{32} tensor component was higher for the 532 nm wavelength and less for the 1064 nm nanosecond laser pulses (see Fig. 4). This indicates on the substantial influence of the absorption edge in the observed photoinduced dependences.

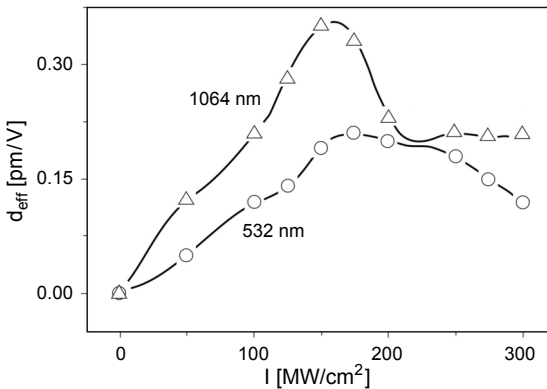


Fig. 4. Photoinduced piezoelectric efficient d_{23} coefficient at different photoinducing wavelengths for fullerene-doped COANP–polyimide structure.

The performed photoinduced piezooptical experiments have shown that the maximal photoinduced piezooptical effect was achieved for fullerene-doped COANP structure. However, these effects are maximal for the diagonal tensor coefficients (see Fig. 5). For the remaining three structures this effect was at least one order less. Moreover, the illumination by 532 nm gives the photoinduced changes at least 3 times higher (see Fig. 5) which correlates with the photoinduced piezoelectricity. It is interesting that

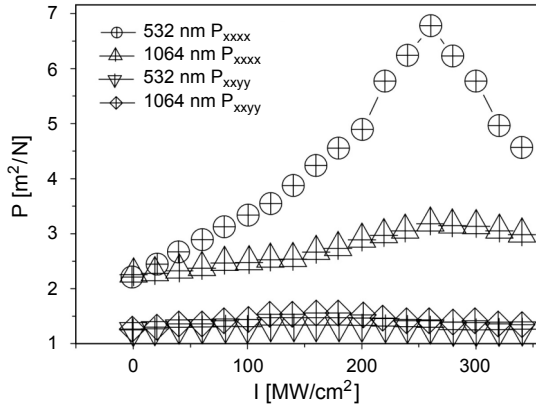


Fig. 5. Photoinduced piezooptical effect for diagonal tensor coefficient at different photoinducing wavelengths for fullerene-doped COANP–polyimide structure.

the maximal effect was observed at power density equal to about 260 MW/cm². At higher intensities there occurs some material's photodestruction.

The relaxation times of the effect do not exceed 6 minutes and the process is completely reproducible during many cycles. The existence of the effect for fullerene-doped COANP–polyimide structure may be caused by the existence of an effective charge transfer which is demonstrated by the absorption spectra presented in Fig. 3 together with the specific contribution of the electron–phonon interaction. It is well-known that the third-order nonlinear piezooptical effects as well as other third-order nonlinear optical susceptibilities are very sensitive to the contribution of the electron–phonon interactions [14, 15]. Additionally, very crucial are interfaces separating the polymers and the embedded chromophores [16, 17]. It is caused by some fluttering of the delocalized states due to the low-dimensional periodicity [18] and electron–phonon anharmonicities [19] together with the influence of the multi-photon processes [20].

4. Conclusions

The photoinduced piezooptical effect was discovered under the influence of the optical treatment by the 1064 nm nanosecond and its second harmonic generation. Moreover, the illumination by 532 nm shows that the photoinduced changes are at least 3 times higher. It is interesting that the maximal effect was observed at power density equal to about 260 MW/cm². At higher processes, the process is less due to the multi-photon excitations. The photoinduced piezoelectrics for the d_{32} tensor component was higher for the 532 nm wavelength and less for the 1064 nm nanosecond laser pulses what indicates on the substantial influence of the absorption edge in the observed photoinduced dependences. The observed effect is a consequence of the substantial

contribution of the photoexcited phonon subsystem. The comparison with the similar chromophore confirms a principal role of the π -conjugated charge transfer due to the interaction with an electron–phonon subsystem.

References

- [1] WANG Y., HERRON N., CASPER J., *Bucky ball and quantum dot doped polymers: a new class of optoelectronic materials*, Materials Science and Engineering B **19**(1–2), 1993, pp. 61–66.
- [2] ROBERTSON J., *Realistic applications of CNTs*, Materials Today **7**(10), 2004, pp. 46–52.
- [3] WEI LEE AND HSU-CHIH CHEN, *Diffraction efficiency of a holographic grating in a liquid-crystal cell composed of asymmetrically patterned electrodes*, Nanotechnology **14**(9), 2003, pp. 987–990.
- [4] BUCHNEV O., DYADYUSHA A., KACZMAREK M., RESHETNYAK V., REZNIKOV YU., *Enhanced two-beam coupling in colloids of ferroelectric nanoparticles in liquid crystals*, Journal of the Optical Society of America B **24**(7), 2007, pp. 1512–1516.
- [5] GRISHINA A.D., LICEA-JIMENE L., PERESHIVKO L.YA., KRIVENKO T.V., SAVEL'EV V.V., RYCHWALSKI R.W., VANNIKOV A.V., *Infrared photorefractive composites based on polyvinylcarbazole and carbon nanotubes*, High Energy Chemistry **40**(5), 2006, pp. 341–347.
- [6] KAMANINA N.V., EMANDI A., KAJZAR F., ATTIAS A.-J., *Laser-induced change in the refractive index in the systems based on nanostructured polyimide: comparative study with other photosensitive structures*, Molecular Crystals and Liquid Crystals **486**(1), 2008, pp. 1–11.
- [7] KAMANINA N.V., SEROV S.V., SHURPO N.A., LIKHOMANOVA S.V., TIMONIN D.N., KUZHAVOV P.V., ROZHKOVA N.N., KITYK I.V., PLUCINSKI K.J., USKOVIC D.P., *Polyimide-fullerene nanostructured materials for nonlinear optics and solar energy applications*, Journal of Materials Science: Materials in Electronics **23**(8), 2012, pp. 1538–1542.
- [8] JIN YAN, MEIZI JIAO, LINGHUI RAO, SHIN-TSON WU, *Direct measurement of electric-field-induced birefringence in a polymer-stabilized blue-phase liquid crystal composite*, Optics Express **18**(11), 2010, pp. 11450–11455.
- [9] SUTTR K., HULLIGER J., GUNTER P., *Photorefractive effects observed in the organic crystal 2-cyclo-octylamino-5-nitropyridine doped with 7,7,8,8-tetracyanoquinodimethane*, Solid State Communications **74**(8), 1990, pp. 867–870.
- [10] LEYDERMAN A., CUI Y., *Electro-optical characterization of a 2-cyclo-octylamino-5-nitropyridine thin organic crystal film*, Optics Letters **23**(12), 1998, pp. 909–911.
- [11] KAMANINA N.V., BARRIENTOS A., LEYDERMAN A., CUI Y., VIKHNIN V., VLASSE M., *Effect of fullerene doping on the absorption edge shift in COANP*, Molecular Materials **13**(1–4), 2000, pp. 275–280.
- [12] KAMANINA N.V., *Peculiarities of optical limiting effect in π -conjugated organic systems based on 2-cyclooctylamino-5-nitropyridine doped with C_{70}* , Journal of Optics A: Pure and Applied Optics **3**(5), 2001, pp. 321–325.
- [13] KAMANINA N.V., PLEKHAHOV A.I., *Mechanisms of optical limiting in fullerene-doped π -conjugated organic structures demonstrated with polyimide and COANP molecules*, Optics and Spectroscopy **93**(3), 2002, pp. 408–415.
- [14] KITYK I.V., KASPERCZYK J., SAHRAOUI B., YASINSKII M.F., HOLAN B., *Low temperature anomalies in polyvinyl alcohol photopolymers*, Polymer **38**(19), 1997, pp. 4803–4806.
- [15] SAHRAOUI B., DERKOWSKA B., KRYZA A., KITYK I.V., *The IR photoinduced changes in the Y–Ba–Cu–O thin films*, Optica Applicata **31**(2), 2001, pp. 445–451.
- [16] KITYK I. V., MAKOWSKA-JANUSIK M., GONDEK E., KRZEMINSKA L., DANIEL A., PLUCINSKI K.J., BENET S., SAHRAOUI B., *Optical poling of oligoether acrylate photopolymers doped by stilbene-benzoate derivative chromophores*, Journal of Physics: Condensed Matter **16**(3), 2004, pp. 231–239.
- [17] KOSCIEN E., SANETRA J., GONDEK E., JAROSZ B., KITYK I.V., EBOUHE J., KITYK A.V., *Optical poling of several halogen derivatives of pyrazoloquinoline*, Optics Communications **242**(4–6), 2004, pp. 401–409.

- [18] KITYK I.V., KASSIBA A., PLUCINSKI K., BERDOWSKI J., *Band structure of the large-sized SiC nano-composites*, Physics Letters A **265**(5–6), 2000, pp. 403–410.
- [19] BUTTNER N., *Some Problems of Electron–Phonon Anharmonicities in Solids*, Munchen Univ. Publishing, 2008, p. 123.
- [20] OZGA K., GONDEK E., DANIEL A., CHACZATRIAN K., *Optical poling of oligoether acrylate photopolymers doped by 1-H-pyrazolo[3,4-b]quinolines derivative chromophores*, Optics Communications **231**(1–6), 2004, pp. 437–446.

*Received October 5, 2012
in revised form November 21, 2012*