ISSN 1407-7353 MATERIAL SCIENCE AND APPLIED CHEMISTRY 2008-7353
MATERIĀLZINĀTNE UN LIETIŠĶĀ ĶĪMIJA

THE TRANS-CIS PHOTOISOMERIZATION POSSIBILITY OF STILBENE AZOCOMPAUNDS BY RED LIGHT OF HE-NE LASER

TRANS-CIS IZOMERIZĀCIJAS IESPĒJAMĪBA STILBĒNA UN AZOBENZOLA ATVASINĀJUMĀ ZEM HE-NE LĀZERA STAROJUMA IETEKMES

Dmitry Saharov, PhD student, M. Sc. Ing.
Riga Technical University, Faculty of Material Science and Applied Chemistry
Adress: Azenes 14/24, LV-1048, Riga, Latvia
E-mail: sda@inbox.lv

Andris Ozols, professor, Dr. habil. Sc. Phys.
Riga Technical University, Faculty of Material Science and Applied Chemistry, Division of Radiation Engineering Physics
Address: Azenes 14/24, LV-1048, Riga, Latvia
Phone: +371 7089456, Fax: +371 7089074
E-mail: aozols@latnet.lv

Valdis Kokars, profesor, Dr. Sc. Chem.
Riga Technical University, Faculty of Material Science and Applied Chemistry, Chair of chemistry.
Address: Azenes 14/24, LV-1048, Riga, Latvia
Phone: +371 7615592, Fax: +371 7901460
E-mail: vkokars@ktf.rtu.lv

Valdis Kampars, dean of Faculty of Material Science and Applied Chemistry, Professor, Dr. habil. Chem.,
Address: Azenes 14/24, LV-1048, Riga, Latvia
Phone: +371 7089224, Fax: +371 7901460
E-mail: kampars@ktf.rtu.lv

Gundars Mezinskis, profesor, Dr. habil. Sc. Ing.
Riga Technical University, Faculty of Material Science and Applied Chemistry
Address: Azenes 14/24, LV-1048, Riga, Latvia
Phone: +371 67089141
E-mail: gundarsm@ktf.rtu.lv

Ansis Maleckis, MS student, BS.
Riga Technical University, Faculty of Material Science and Applied Chemistry
Adress: Azenes 14/24, LV-1048, Riga, Latvia
E-mail: maleckisa@inbox.lv

Arturs Pludons, PhD student, M. Sc. Ing.
Riga Technical University, Faculty of Material Science and Applied Chemistry
Adress: Azenes 14/24, LV-1048, Riga, Latvia
E-mail: yyy@ktf.rtu.lv

Martins Rutkis, leading researcher, Dr. Sc. Phys.
Institute of Solid State Physics, University of Latvia
Address: Kengaraga 8, LV-1063, Riga, Latvia
E-mail: martins.rutkis@cfi.lu.lv

Key words:* *trans-cis photoisomerization, stilbene, azobenzene, surface relief grating, red laser, chromophore photoorientation.

Introduction

Structure and chemical composition of organic materials can be widely changed so that materials with well defined properties can be produced. Azocompounds are among the most efficient materials for holographic recording [1,2,3] which we have studied, also in previous papers [4,5]. Commonly, blue and green spectrum ranges are used for recording in these materials because absorption spectra of azocompaunds have maxima there. In this case *trans-cis-trans* transformation [1] of material under laser radiation takes place. In the red spectrum range absorption is considerably lower yet the recording is possible [4, 5]. Mechanism of such recording is unclear yet this fact creates motivation for further researches. Discovery of efficient materials for information optical recording in the red part of spectrum will also allow using cheaper equipment and producing volume holographic optical elements with better quality. In this paper we have experimentally studied the material relaxation effect on the holographic properties of stilbene azobenzene derivatives when the recording and readout was made by the red light. It is found that material relaxation has strong and nonmonotonic influence on holographic recording efficiency. Besides, surface relief gratings have been recorded by a red light for the first time, to our knowledge.

Materials

The structural formula of the most efficient studied stilbene azobenzene films and their full chemical designation are given in Fig.1.These results are presented here. Films were brought on the glass substrates by spin-coating. Chromophore was dissolved in dichloromethane. A drop of the solution was placed on the rotating glass plate where it was distributed rather evenly. After the evaporation of dichloromethane the film has been formed.

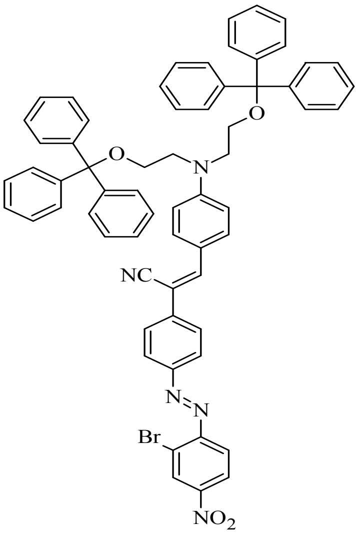


Fig.1. *Structure formula of the studied most efficient material 3-{4-[bis(2-trityloxyethyl)amino]fenyl}-2-{4-[(2-bromo-4-nitrophenyl)diazenyl]phenyl}acrylonitrile*

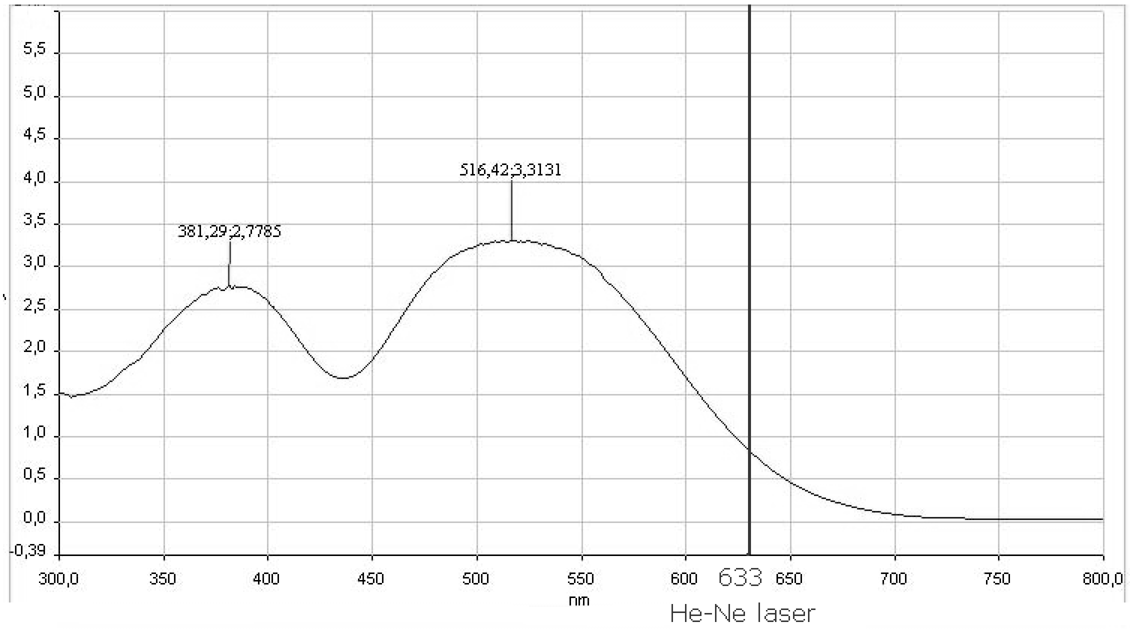


Fig.2. *Absorption spectra of the sample. Red line shows wavelength of the laser. Maximums of absorption are shifted in comparison with azobenzene to be red light sensitive. The absorption spectra of the samples were measured before the recording.*

Methods

The main measurements were made at the holographic setup shown in Fig.4. Optical elements were placed on the massive table with purpose to avoid vibrations. Laboratory windows were closed by dark nontransparent (for optic spectral range) material. Laser ЛГН-222 was used for the recording and readout at λ=632.8 nm. Optical scheme is shown on Fig. 4.

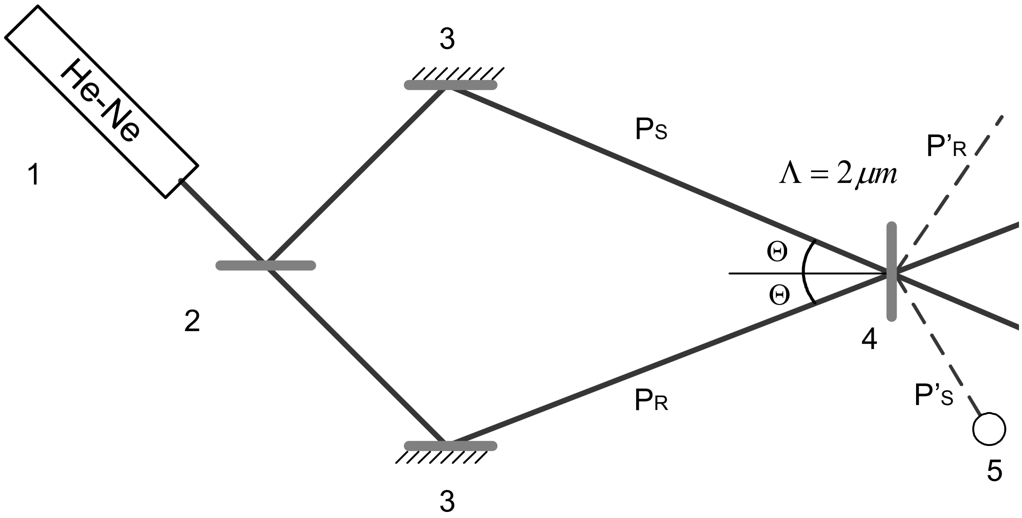


Fig. 3. *Experimental set-up. 1- laser; 2 – beam splitter; 3 - mirrors; 4 – sample; 5 – photodetector.*

Diffraction efficiency (DE) could not be measured directly due to fast changes of diffracted beams' power that were observed during exposure. Measurements were made without interruption of one beam. So, measurements of self-diffraction efficiency (SDE) were made in real-time mode. Light power measurements were made by “Gentec” power meter (Canada). The measurement results were stored in its memory and processed later. This registration method allowed to measure fast SDE changes during the exposure. The magnitude was found according to the formula:

$$SDE = \frac{P_d(k=-2, l=-1)}{P_s}, \qquad (1)$$

where $P_d(k=-2,l=-1)$ is sum of first-order diffracted power of one beam and second-order diffracted power of other beam (see Fig.5), P_S is the incident readout light power.

Non-focused laser beams with $1/e^2$ diameter equal 1.5 mm were directed to the same point on the sample and formed interference pattern there. Holographic grating period was 2 μm. Period was defined by the Θ angle as

$$\Lambda = \frac{\lambda}{2\sin\Theta}, \qquad (2)$$

where Λ – holographic grating period, λ – wavelength of laser radiation, Θ – angle of incidence of the laser beam.

Graphs were created using measurements results. It shows dynamics of self-diffraction efficiency during exposure time. For the every measurement specific recording energy W_{max} was calculated according to the formula

$$W_{\max} = \frac{It}{\eta_{\max}}, \qquad (3)$$

where I – recording light intensity, t – exposure time corresponding to η_{max}, η_{max} – maximal diffraction efficiency.

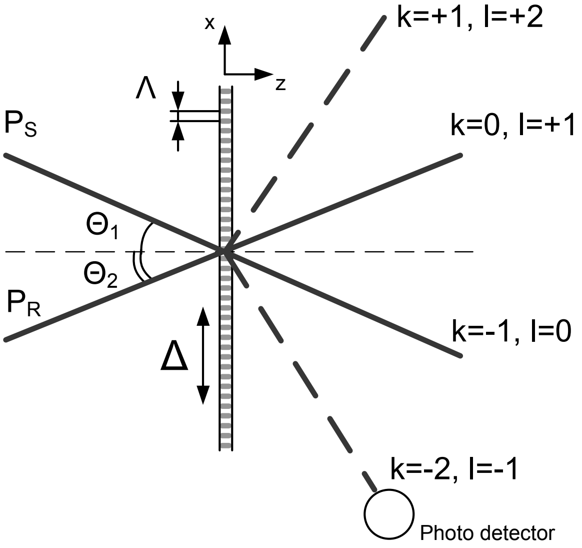


Fig.4. *Scheme of recording process. P_S and P_R – incident laser beams, $\Theta_1 = \Theta_2$ – angles of incidence of the beams, k – diffraction orders of P_R beam, l – diffraction orders of P_S beam, Λ=2μm – period of holographic grating, Δ – grating displacement due to set-up*

instability or (and) movement of molecules. $\Delta\frac{2\pi}{\Lambda} = \Phi_S - \Phi_R$, *where* Φ_S *and* Φ_R *are phases of zero-order diffractions of* P_S *and* P_R *beams accordingly.*

The average intensity was defined by the formula

$$I = \frac{4(P_R + P_S)}{\pi d^2}, \tag{4}$$

where d – $1/e^2$ laser beam diameter.
Self-diffraction efficiency (SDE) was used to estimate diffraction efficiency (DE). According to the calculations made on the basic of thin hologram theory [6] SDE and DE are related by the expression

$$SDE = DE_{(-1)} + \frac{P_R}{P_S} DE_{(-2)} + 2\sqrt{\frac{P_R}{P_S} DE_{(-1)} DE_{(-2)}} \cos(\Phi_S - \Phi_R + \Phi_{S(-1)} - \Phi_{R(-2)}), \tag{5}$$

where P_R and P_S are the incident beams with equal power, $DE_{(-1)}$ is the minus first-order diffraction efficiency, $DE_{(-2)}$ is the minus second-order diffraction efficiency of P_R beam, Φ_S and Φ_R are the phases of the zero-order diffracted P_S and P_R beams accordingly, $\Phi_{S(-1)}$ and $\Phi_{R(-2)}$ are phase of the first-order diffracted wave P_S and the phase of the minus second-order diffracted wave P_R.

The first term of the sum in the expression is diffraction efficiency that needs to be estimated. The third term describes the instability of induced grating, that can be caused by equipment imperfection or (and) molecules moving under light influence.

Results and discussion

The measurement results are presented in Figs. 5 to 7. The maximum SDE value is 4.74%. Small dips are due to the nonmonotonic nature of the chromophore photoorientation counteracted by thermal back reactions. Large dips are due to the small instabilities of the recording setup causing small shifts of the recording interference pattern with respect to the recorded grating. This behavior was repeatable and follows from the expression (5).

Fig. 6 shows that surface relief grating (SRG) is recorded together with the refraction and absorption gratings. SRG was stable during a year. This is the first SRG recording by a red light, to our knowledge. In contrast, DE and SDE varied in the course of storage. The conclusion about refraction and absorption gratings is supported by the DE calculations of SRG according to the formula

$$\eta = \frac{\tau}{3}\left[\frac{\pi(n-1)d_{1\max}}{\lambda\cos\theta_i}\right]^2, \tag{6}$$

where τ is the transmittance of the grating, n – its average refractive index, d_{1max} is the amplitude of thickness modulation, λ – the readout wavelength, θ_i is the readout beam incidence angle inside the medium. This formula (6) was derived by us on the basis of thin hologram theory [6]. The calculation at $\tau = 0.398$, $n = 1.5$, $d_{1max} = 113$ nm, $\lambda = 633$ nm, $\cos\theta_i = 1$ have given $\eta = 1.04$ % which is less than the maximum SDE value of 4.74 %.

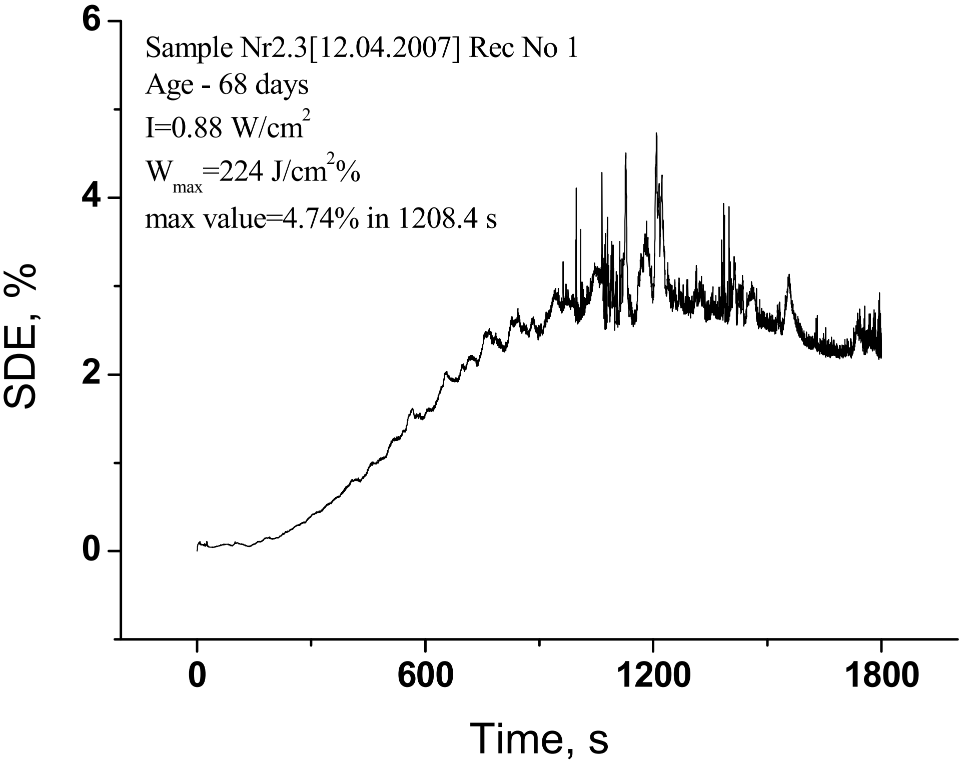
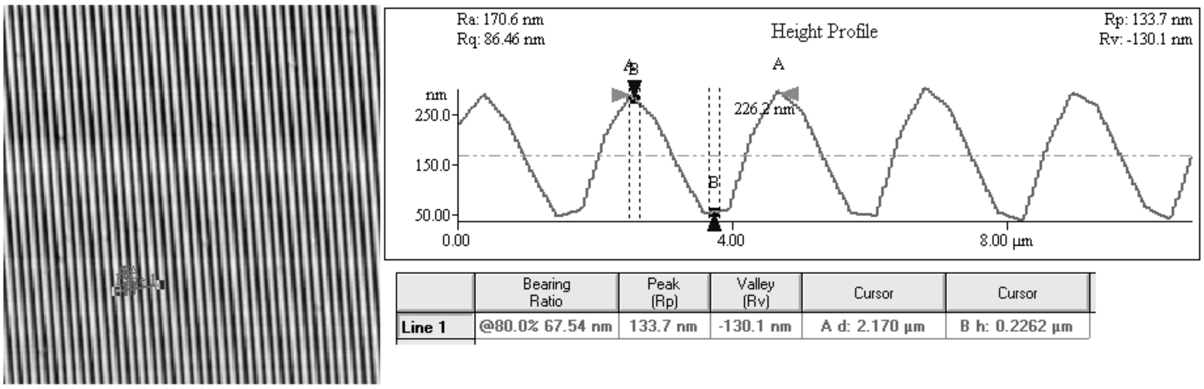


Fig.5. *Self-diffraction efficiency (SDE) changes during the exposure.*



	Bearing Ratio	Peak (Rp)	Valley (Rv)	Cursor	Cursor
Line 1	@80.0% 67.54 nm	133.7 nm	-130.1 nm	A d: 2.170 µm	B h: 0.2262 µm

Fig.6. *Surface relief and profile in the centre area of the recording. Amplitude between highest and lowest points is approximately 226 nanometers.*

The changes of absorption spectra during the holographic recording are shown in Fig. 7. From Fig.7 we can see prevalent absorption decrease. This figure shows average absorption changes in the area approximately 25 mm^2 where 25 records were written near each other.

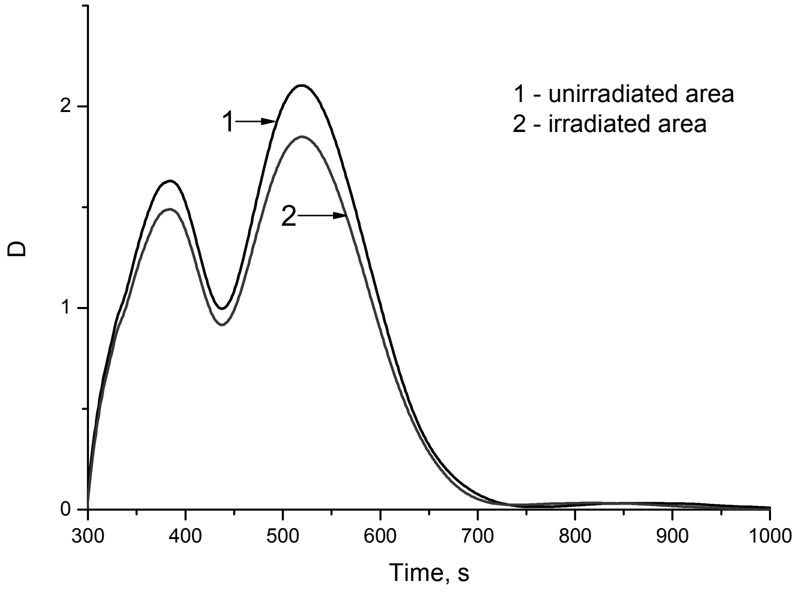


Fig.7. *Optical density versus wavelength. Measurements performed by PERKIN ELMER Instruments Lambda35 UV-VIS spectrometer. There were made 25 records with a diameter of 1.93 mm in the area 5x5 mm in the sample because of the spectrometer's measuring beam low positioning precision.*

Fig.7 shows that optical density has decreased almost uniformly, except a little increase in the long wavelength part after 700 nm. This is in contrast with known *trans-cis* spectral transformations in UV and visible bands [7]. Besides, *cis-trans* back reaction proceeds in time from seconds to hours [7], and, therefore, were finished when the absorption spectra were measured about two months after the recording. Thus we cannot exclude the *trans-cis* photoisomerization but it seems unlikely. Yet, further experiments are needed to make the conclusion about the contribution of photoisomerization. Mostly uniform reduction of the absorbance after recording can be explained by the photodegradation, i.e., by chromophore destruction under irradiation during the recording process. For example, N-N bonds can be broken by 633 nm photons [8]. The photoablation is also possible but it needs recording intensities higher than 1 W/cm^2 [8].

As the calculated diffraction efficiency for surface relief grating only is much smaller than measured experimental diffraction efficiency value, one can conclude that other recording mechanisms apart from photodegradation or photoablation take place. One is the photoorientation mechanism [4,5,8]. Chromophore groups and fragments of molecules that have dipole moments can change their orientations and spatial positions under the influence of the linearly polarized light. As a result, the refraction and absorption indices have been changed. A spatially periodic density modulation accompanying the photodegradation can also contribute.

Summary

Surface relief gratings with the relief change as high as 126 nm have been recorded in organic materials with a red light for the first time. *Trans-cis p*hotoisomerization of azobenzene chromophores, most probably, does not play the main role under 633 nm light irradiation in stilbene azobenzene derivative which we have studied. However, further studies are necessary to give a definite answer. Uniform optical density decrease in UV-VIS spectral region and periodical surface relief (SRG) formation allows supposing that photodegradation of chromophores and/or photoablation are the main SRG recording mechanisms in the studied stilbene azobenzene derivative. They can be accompanied by either the photorientation of chromophores and molecular fragments leading to the simultaneous amplitude-phase holographic grating recording and/or by density modulation.

References

1. Schwartz K 1993 *The Physics of Optical Recording* (Berlin: Springer Verlag) 191 p.
2. Delaire J A and Nakatani K 2000 Linear and nonlinear optical properties of photochromic molecules and materials *Chem Rev.* **100** 1817-1845
3. Rasmussen P H Ramanujam P S Hvilsted S and Berg R H 1999 A remarkably efficient azobenzene peptide for holographic information storage *J.Am. Chem.* **121** 4738-4743
4. Ozols A Kampars V Reinfelde M Kokars V 2003 Hologram recording in azobenzene oligomers *Proc. SPIE* **5123** 102-109
5. Ozols A Kampars V Reinfelde M Kokars V 2005 Structure optimization of azobenzene oligomers for holography *Phys. Stat. Sol.(c)* **1** 673-676
6. Ozols A O 1977 Diffraction efficiency of thin amplutude-phase holograms. *Opt. Spektrosk.* **42**, 168-174.
7. Rau H. Photoisomerization and photoorientation of azobenzenes, in *Photoreactive Organic Thin Films* , edited by Sekkat Z and Knoll W 2002(California, Academic Press) pp.3-40.
8. Oliveira O N, Kumar L L Tripathy S K. Surface-relief gratings on azobenzene-containing films, in *Photoreactive Organic Thin Films* , edited by Sekkat Z and Knoll W 2002(California, Academic Press) pp.429-483.

D. Saharovs, A. Ozols, V. Kokars, V. Kampars, G. Mežinskis, A. Maļeckis, A. Plūdons, M. Rutkis. Trans-cis izomerizācijas iespējamība stilbēna un azobenzola atvasinājumā zem He-Ne lāzera starojuma ietekmes. *Dotajā rakstā eksperimentāli pētīta trans-cis fotoizomerizācijas iespējamā loma virsmas reljefa režģu ierakstā stilbēna azobenzola atvasinājumos, kad ieraksts un nolase tika veikti ar sarkano 633 nm gaismu. Konstatēts , ka materiāla relaksācijai ir stingra nemonotona ietekme uz hologrāfiskā ieraksta efektivitāti un ka ierakstās ne vien virsmas reljefa režģi, ber arī tilpuma režģi. Iegūtie rezultāti neļauj secināt, ka trans-cis fotoizomerizācijas spēlē galveno lomu. Izdarīts secinājums, ka hromoforu fotodegradācija un fotoorientācija ir galvenie ieraksta mehānismi pētītajos materiāos.*

Saharov D., Ozols A., Kokars V., Kampars V., Mezhinskis G., Maleckis A., Pludons A., Rutkis M. The trans-cis photoisomerization possibility of stilbene azocompaunds by red light of He-Ne laser. *In this paper we have experimentally studied the possibility of trans-cis photoisomerization effect as the origin of photoinduced surface relief gratings inf stilbene azobenzene derivatives when the recording and readout was made by the red light. It was alsos found that material relaxation has strong and nonmonotonic influence on holographic recording efficiency and that volume holographic gratings are also recorded.. Trans-cis photoisomerization of azobenzene chromophores was not found to play the main role under 633 nm light irradiation in stilbene azobenzene derivativse which we have studied. The obtained experimental results allow supposing that photodegradation and photoorientation of chromophores are the main recording mechamisms in the studied material.*

Сахаров Д., Озолс А., Кокарс В., Кампарс В., Межинскис Г., Малецкис А., Плудонс А., Руткис М. Возможность транс-цис изомеризации в производном от стилбена и азобензола соединении под воздействием излучения He-Ne лазера. *В данной статье экспериментально исследована возможная роль транс-цис изомеризации в записи поверхностной рельефной решётки в производных азобензола и стилбена, когда запись и считывание производились красным светом с длиной волны 633нм. Определено,*

что релаксация вещества имеет сильное немонотонное влияние на эффективность голографической записи и что записываются не только поверхностные рельефные решётки, но и объёмные решётки. Достигнутые результаты не позволяют предполагать, что транс-цис изомеризация играет в процессе записи главную роль. Сделан вывод, что главными механизмами записи в исследуемых образцах являются фотодеградация и фотоориентация хромофоров.