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MECHANISM OF OPTICAL NONLINEARITY IN "LYOTROPIC LIQUID CRYSTAL — VIOLOGEN" SYSTEM

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Abstract. *In the present work we analyze the characteristics of holographic grating recording and consider a mechanism of optical nonlinearity in the lyotropic liquid crystal (LLC) — viologen samples. Taking into account structural and electrooptical properties of the admixture molecules it is possible to suggest that the recording is realized due to the change of polarizability of π-electron system of coloured viologen derivatives under the action of laser radiation. The main nonlinear optical parameters such as nonlinear refraction coefficient n2, cubic nonlinear susceptibility χ(3), and hyperpolarizability γ were calculated.*

Keywords: diffraction efficiency; lyotropic liquid crystals; nonlinear optics; polarizability; viologens.

1. Introduction

The diffraction grating recording on LLC-viologen composites was realized and investigated in the works [1, 2].

Registered values of the diffraction efficiency in a self-diffraction regime considerably exceeded the residual thermal gratings efficiency. Accordingly, the mechanism of holographic recording in LLC-viologen samples couldn't be explained by a thermal nonlinearity which is peculiar to the most liquid crystalline materials. Most likely it relates to nonlinear effects taking place in admixture molecules.

2. Analysis of investigations and publications

Nonlinear optical properties of liquid crystal materials appear in the case of absorptive mediums and relate to the action of laser radiation on absorptive centers.

In the work [5] diffraction grating recording on the samples of smectic glasses of Cobalt alkanoates is explained by a laser-induced nonlinear polarizability of π-electrons of carboxyl groups of Cobalt complexes. Investigated nonlinear optical properties and holographic recording in bilayer cells "lyotropic ionic liquid crystal — polymethine dye" are caused by resonance nonlinearity [4].

The **aim** of the present work is to clarify the mechanism of optical nonlinearity and holographic recording for the samples of lyotropic liquid crystal with viologen admixtures, and to determine main non-linear optical parameters of the investigated samples.

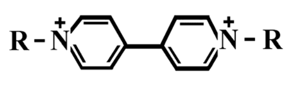
3. Materials and methods

Lyotropic liquid crystal was formed when mixing powder of a Potassium caprylate with water in 1:1 weight proportion was doped by admixtures of two types of viologens: $HD^{2+}2Br^{-}$ and $CED^{2+}2Cl^{-}$. The viologens differ in substitutes at Nitrogen atoms and counterions [1]. Viologen content in the samples came to 2% by weight.

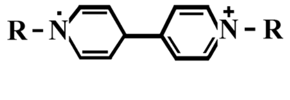
It is determined [1] that an external electric field application to the cells filled with LLC-viologen composite leads to the colouration of the samples, which is caused by viologens reduction near cathode. As a result initially homogeneous samples undergo a separation into a coloured layer of viologen reduction products and a liquid crystal layer.

Depending on the value of an applied electric field viologen molecules could be found in three forms:

— viologen dication (U = 0 V, sample is colourless):

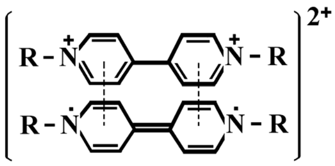


— radical cation (U = 2–2,5 V, sample is blue), formed by one-electron reduction of the initial dication:



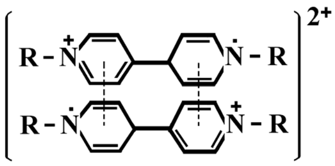
— dimer (U = 4 V, sample is red).

Dimerization with equal probability could pass in two ways: after the interaction between the initial dication and the molecule undergone two-electron reduction:



,

or after the interaction between two radical cations:



where R — substitutes at Nitrogen atoms.

For the $HD^{2+}2Br^{-}$

$R = C_7H_{15}$,

for $CED^{2+}2Cl^{-}$

$R = (CH_2)_2COOH$.

Holographic diffraction grating recording was obtained for the LLC samples containing admixtures of viologens $HD^{2+}2Br^{-}$ and $CED^{2+}2Cl^{-}$.

The recording was realized on the coloured samples after the application of an electric field with voltage value of U = 3-4 V.

That is, in both cases viologen dimers served as absorption centers. The wavelength of a recoding laser radiation equals to λ = 539,8 nm and thus falls within the absorption band of dimers (λ = 515 nm) [1]. The recording took place in a thin coloured layer of viologen reduction products, diffraction efficiency of the recorded gratings reached 0,2%.

4. Cubic nonlinear susceptibility

It is known that organics whose molecules contain delocalized π-electrons can exhibit the effect of nonlinear polarization in the intense laser radiation field in the case when polarization value depends nonlinearly on the external electric field intensity [7, 8, 9].

Second-order dependence of the diffraction efficiency on the laser radiation intensity obtained experimentally [1] points at the cubic nonlinear susceptibility of LLC-viologen systems.

For cubic nonlinear optical media refractive index n depends linearly on the laser radiation intensity I:

$$n(I) = n_0 + \Delta n(I) = \\ = n_0 + \frac{\chi^{(3)}}{\varepsilon_0\, c\, (n_0)^2} I = \\ = n_0 + n_2 I,$$

$$I = \frac{\varepsilon_0\, c \sqrt{\frac{\varepsilon}{\mu}}\, E^2}{2},$$

where n_0 — an average refractive index,;

$\chi^{(3)}$ — a cubic nonlinear susceptibility;

ε_0 — an electric constant;

n_2 — a coefficient of nonlinear refraction;

ε — a permittivity;

μ — a magnetic susceptibility;

E — a value of an external electric field intensity.

According to the nonlinear experiment scheme [1] the spatial modulated laser radiation (the result of two coherent laser beams interference) falls onto the investigated medium. The intensity of the radiation is given by expression:

$$I = (I_1 + I_2)(1 + m\cos(\frac{2\pi}{\Lambda}x)), \\ m = \frac{2\sqrt{I_1 I_2}}{I_1 + I_2}, \quad (1)$$

where I_1, I_2 — the intensities of laser beams which interfere on the investigated sample;

m — the modulation depth;

Λ — interference pattern period,;

x — the direction of intensity modulation.

In consequence of nonlinear optical medium response spatially periodic intensity distribution (1) causes the appearance of refractive index grating.

Recording laser beams diffract on this grating, i.e. the recording passes in a self-diffraction regime.

For a thin grating the diffraction efficiency η is defined by the following expression [3]:

$$\eta = T\left(J_1(\frac{2\pi\, d\, n_2\, m\, I}{\lambda})\right)^2 \approx \\ \approx T\left(\frac{\pi\, d\, n_2\, m\,(I_1 + I_2)}{\lambda}\right)^2, \quad (2)$$

where T — transmission;

J_1 — the first order Bessel function;

d — the depth at which nonlinear phase incursion occurs (in our case it is the thickness of a photosensitive layer of viologen reduction products);

λ — wavelength of a recording laser radiation.

The nonlinear refraction coefficient is determined from the expression (2) as following:

$$|n_2| = \frac{\lambda}{\pi\, d\, m\,(I_1 + I_2)}\sqrt{\frac{\eta}{T}}.$$

The coefficient of nonlinear refraction n_2 and the corresponding value of cubic nonlinear susceptibility $\chi^{(3)}$ are important macroscopic characteristics of a medium's cubic optical nonlinearity. From the experimental dependence

$$\eta = f(I^2)$$

it is possible to evaluate the coefficient of nonlinear refraction and then, the hyperpolarizability γ:

$$\gamma = \frac{\chi^{(3)}}{N L^4} ,$$

where N — a concentration of molecules.

The local field factor L and $\chi^{(3)}$ value were calculated using following expressions:

$$L = \frac{n_0^2 + 2}{3} ;$$

$$\chi^{(3)} = n_2 \, \varepsilon_0 \, c \, (n_0)^2 ;$$

$$\chi^{(3)}(esu) = \frac{9}{4\pi} 10^8 \chi^{(3)}(CI) .$$

Determined values of nonlinear optical parameters n_2, $\chi^{(3)}$ and γ are given in the Table.

Nonlinear optical parameters
of LLC-viologen composites

Nonlinear optical medium	η, %	n_2, $cm^2 \cdot W^{-1}$	$\chi^{(3)}$, esu	γ, esu
$CED^{2+}2Cl^-$ (dimers)	0,19	$1{,}8 \cdot 10^{-10}$	$0{,}8 \cdot 10^{-8}$	$1{,}2 \cdot 10^{-28}$
$HD^{2+}2Br^-$ (dimers)	0,19	$3 \cdot 10^{-10}$	$1{,}3 \cdot 10^{-8}$	$2{,}7 \cdot 10^{-28}$

All the data are given in esu system, which is widely used in the nonlinear optics. Also there is the transition expression between esu and CI systems.

Obtained high values of nonlinear susceptibility ($\chi^{(3)} \sim 10^{-8}$ esu) for viologen dimers and hyper-polarizability ($\gamma \sim 10^{-28}$ esu) are close to the best characteristics of the organic dyes [7, 8, 9].

5. Discussion

High values of the hyperpolarizability could be caused by both near-resonance excitation and accumulation of delocalized electron density in the viologen reduction products (dimers) in comparison with the initial molecules.

As it is seen from the structural formula viologen dication contains two dipyridilium rings with two Nitrogen atoms. The last ones carry positive charges, which in the most cases reduce delocalization of π-electron cloud of the molecules [6].

Radical cation contains only one uncompensated positive charge; that is its delocalized π-electron density increases in comparison with the initial viologen dication. π-electron delocalization increases even greater for dimers.

As a result the polarization of dimers in an electric field of laser radiation is the largest. The last fact is proved by the experiment: the highest diffraction efficiency was registered for LLC-viologen samples containing viologens in the state of dimers. Corres-pondingly the hyperpolarizability γ is also the highest.

For the transparent (without electric field appli-cation) samples containing initial viologen dications we didn't register holographic grating recording [1].

The important factor, which also facilitates increase of the diffraction efficiency and hyperpolarizability is that the wavelength of an exciting laser radiation (λ = 539,8 nm) falls within an absorption band of the recording medium. It was determined [1] that absorption maximum of dimers lies is near λ = 515 nm.

Therefore the effect of resonance enhancement plays the significant role for the LLC samples containing viologens in the state of dimers.

It is worth noting that holographic diffraction grating recording was also realized for blue-coloured radical cations of viologens $HD^{2+}2Br^-$. Their absorption maximum corresponds to the wavelength λ = 605 nm. The diffraction efficiency registered for radical cations appeared to be two times smaller than the one of dimers. In our opinion it is concerned with lesser resonance effect.

6. Conclusions

1. We suggested the mechanism of the optical nonlinearity of LLC-viologen samples taking into account previously obtained characteristics of holographic recording on investigated composites. This mechanism is concerned with nonlinear (cubic) polarization of π-electron cloud of viologen derivatives.

2. Based on the experimental data we calculated main nonlinear optical parameters of LLC-viologen composites, such as coefficient of nonlinear refraction n_2, nonlinear susceptibility $\chi^{(3)}$, and hyperpolarizability γ. For all the obtained data we observed an order-of-magnitude agreement with the best characteristics for organics in the presence of the resonance excitation.

3. It was established that high values of hyper-polarizability of LLC-viologen systems are stipulated by resonance excitation and depend on the electron density delocalization degree of viologen reduction products.

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Запропоновано механізм оптичної нелінійності в зразках ліотропного рідкого кристалу з домішками віологенів, який полягає в зміні поляризовності π-електронної системи домішкових молекул під впливом лазерного випромінювання. Визначено основні нелінійно-оптичні параметри досліджуваних зразків.

Ключові слова: віологени; дифракційна ефективність; ліотропні рідкі кристали; нелінійна оптика; поляризовність.

А.Б. Бордюг[1], А.П. Полищук[2]. Механизм оптической нелинейности системы «лиотропный жидкий кристалл — виологен»

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Предложен механизм оптической нелинейности в образцах лиотропного жидкого кристалла с примесями виологенов, который заключается в изменении поляризуемости π-электронной системы примесных молекул под действием лазерного излучения. Определены основные нелинейно-оптические параметры исследуемых образцов.

Ключевые слова: виологены; дифракционная эффективность; лиотропные жидкие кристаллы; нелинейная оптика; поляризуемость.

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