

TEMPORAL EVOLUTION OF THE LASER RECORDING OF GRATINGS IN DNA-CTMA-Rh610 FILMS

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Abstract. In this paper, the laser recording of thin diffraction gratings in deoxyribonucleic acid (DNA) – cetyltrimethyl-ammonium chloride (CTMA) surfactant doped with Rhodamine 610 (Rh610) films is experimentally investigated. The diffraction efficiency of the gratings induced in dye-doped DNA films by the interference of two Ar laser beams at 514.5 nm wavelength is monitored using a He-Ne probe beam (633 nm wavelength). Considering the efficiency experimental data, the temporal evolution of the phase change during the grating recording is modeled in the frame of the Raman-Nath diffraction theory. These results are important for applications of dye-doped DNA films in nonlinear photonics.

Key words: laser induced diffraction gratings, Raman-Nath diffraction, dye-doped DNA, Rhodamine 610.

1. INTRODUCTION

The deoxyribonucleic acid (DNA) is intensively studied in the last years, due to its promising applications in organic photonics and organic opto-electronics [1–6]. DNA-based bio-photonics materials are biodegradable, are extracted from renewable resources, in particular the waste of food processing industry, by modern ecological technologies. The optical properties of DNA-based materials can be tailored for targeted applications by an appropriate functionalization. The DNA biopolymer has a wide range of transparency in visible and near-infrared [7], has a good thermal stability and represents an interesting matrix for photosensitive molecules. In comparison with synthetic polymers, the particular supramolecular double-stranded helical structure of DNA molecules [8, 9] offers a high free volume and a kind of protection for embedded photosensitive molecules, with significantly lower kinetic chemical and photo-thermal degradation constants. This specific environment can lead to an increase of the quantum efficiency of the embedded chromophores, compared with other matrices, as reported by several

research groups [10–13]. It was demonstrated that the DNA complexes represent good matrices for lasing of embedded dyes [14, 15]. Also, the structure of DNA molecules [8, 9] can be used to get sufficiently fast photo-induced response and improved nonlinear optical properties in dye-DNA compounds [16, 17].

In this paper, laser induced diffraction gratings in thin films of DNA doped with Rh610 dye are experimentally investigated and the recording process is analysed. The gratings are recorded by the interference of two Ar laser beams at 514.5 nm wavelength. By monitoring the diffraction efficiency of the gratings with a He-Ne probe beam (633 nm wavelength), the temporal evolution of the light-induced phase change (directly related to the grating recording) is modeled in the frame of the Raman-Nath diffraction theory. For comparison we used a synthetic polymer, poly-methyl methacrylate (PMMA), doped with Rh610 dye.

The optical recording is based on photo-induced processes that modify optical parameters of the investigated material. The investigation of the laser recording of gratings in dye-doped DNA complexes is important for their applications in photonics.

2. THE RAMAN-NATH DIFFRACTION ON THIN PHASE GRATINGS

In two-wave mixing experiments, two mutually coherent laser beams that interfere in a nonlinear optical material induce a grating inside the material, by periodic modulation of its optical properties. The light-induced gratings in nonlinear media can be phase gratings (refractive index and/or relief modulation), amplitude gratings (absorption coefficient modulation) or mixed. The diffraction properties of the induced grating can be probed by the diffraction of other laser beam, or by the diffraction of the recording beams themselves (self-diffraction). The temporal evolution of the light-induced grating can be determined by monitoring the diffraction efficiency of the probe beam.

Our two-wave mixing experiments in the investigated samples were carried out in the Raman-Nath diffraction regime [18–22]. In this regime the angle β between the interfering beams is very small leading to a grating period larger than the sample thickness (“thin” gratings). When the incidence of the interfering beams on the sample is close to normal, the grating period Λ is:

$$\Lambda \cong \lambda / \beta . \quad (1)$$

Specific to the Raman-Nath diffraction regime is the appearance of many diffraction orders when a probe beam is diffracting on the recorded grating. These orders ($\pm 1, \pm 2, \dots$) are symmetrical to the probe beam transmitted through the grating (0^{th} diffraction order). The diffraction regime on the phase gratings induced in a sample of thickness d from a material of which the refractive index n_0 is modulated with the amplitude Δn , is characterized by the values of two

dimensionless parameters, the phase correlation of the diffraction orders, Q , and the amplitude of the phase modulation, $\Delta\Phi$ [22]:

$$Q = 2\pi\lambda d / (n_0\Lambda^2), \quad (2)$$

$$\Delta\Phi = 2\pi\Delta nd / \lambda. \quad (3)$$

Ideally, the values of these parameters must be: $Q \ll 1$ and $Q \cdot \Delta\Phi \ll 1$ for a rigorous description of the diffraction spectrum in the frame of the Raman-Nath diffraction theory. In practice, for $Q \leq 0.5$ and $Q \cdot \Delta\Phi \leq 1$, the intensities of the diffraction orders are predicted sufficiently accurate (very few percents of difference) by the Raman-Nath theory.

In the Raman-Nath diffraction theory, the intensity diffracted in the l^{th} diffraction order is:

$$I_l = TI_R J_l^2(\Delta\Phi), \quad (4)$$

where I_R is the intensity of the reading (probe) beam, T is the transmission of the sample and $J_l(\Delta\Phi)$ is the Bessel function of first kind and l^{th} order, having as argument the amplitude of the phase modulation, $\Delta\Phi$. The intensities of the 1st diffraction order and of the 0th diffraction order (non-diffracted light), respectively, are:

$$I_1 = TI_R J_1^2(\Delta\Phi), \quad (5)$$

$$I_0 = TI_R J_0^2(\Delta\Phi). \quad (6)$$

The diffraction efficiency in the first order is defined as the ration between the intensity diffracted in this order, I_1 , and the intensity transmitted initially through the sample, before of the grating recording, TI_R :

$$\eta_D = I_1 / TI_R. \quad (7)$$

The temporal evolution of the light-induced phase modulation during the recording process in the nonlinear medium, $\Delta\Phi(t)$, determines the temporal dependence of the diffraction order intensities, $I_1(t) \propto J_1^2[\Delta\Phi(t)]$, $I_0(t) \propto J_0^2[\Delta\Phi(t)]$, and of the diffraction efficiency, $\eta_D(t)$, respectively. At initial moment, before the starting of the recording process, the phase modulation $\Delta\Phi(0) = 0$, $J_0^2(0) = 1$ and $I_0(0) = TI_R$. The temporal dependence of the diffraction efficiency can be written as:

$$\eta_D(t) = I_1(t) / I_0(0) = J_1^2[\Delta\Phi(t)]. \quad (8)$$

In experiments, by monitoring $I_1(t)$ and measuring $I_0(0)$, the temporal dependence of the diffraction efficiency can be determined. Taking into consideration a certain mathematical expression for the temporal dependence of the phase modulation, the parameters of this dependence can be determined by fitting the experimental diffraction efficiency curve.

3. EXPERIMENTS ON LASER RECORDING OF GRATINGS IN DNA-CTMA-Rh610 AND PMMA-Rh610 FILMS

3.1. THE SAMPLE PREPARATION

The DNA used to prepare the investigated samples was purchased from Ogata Research Laboratory, Ltd, Chitose, Japan. The samples were prepared according to the procedure described by Rau *et al.* [23]. After sonication, the DNA was washed and mixed with surfactant CTMA for obtaining samples soluble in butanol. The concentration of the DNA-CTMA in butanol was 30 g/l. The obtained DNA-CTMA solutions were functionalized by doping with Rh610 dye. The dye-doping concentration, representing the percentage of the dye mass with respect to the matrix dry mass, was 10 %. For comparison we used other complex based on the synthetic polymer PMMA (soluble in trichloroethane), doped with the same concentration of Rh610. From these solutions, thin films have been obtained by deep coating method. The thickness of the investigated films was $d \approx 20 \mu\text{m}$.

3.2. THE EXPERIMENTAL SETUP

A schematic of the two-wave mixing experimental configuration used for the study of the temporal evolution of grating recording is shown in Fig. 1.

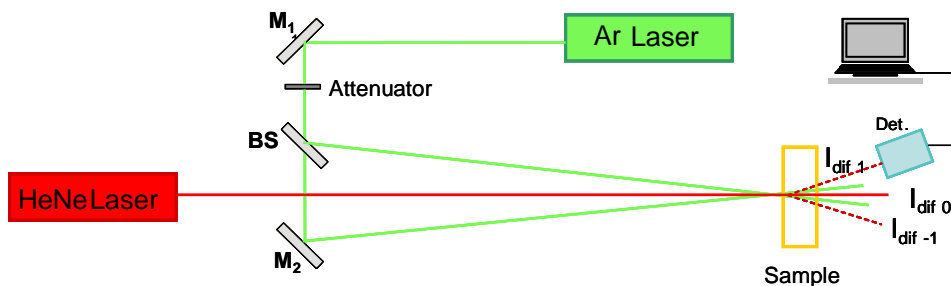


Fig. 1 – The experimental setup used for the study of the temporal evolution of grating recording.

The s-polarized Ar laser beam ($\lambda = 514.5 \text{ nm}$) is divided by the beam splitter (BS) in two beams of approximately equal intensities. They interfere at a small angle ($\beta = 0.0143 \text{ rad}$) in the investigated sample, recording a grating with a period

$\Lambda = 36 \mu\text{m}$. A He-Ne laser beam ($\lambda = 632.8 \text{ nm}$) is probing the diffraction properties of the recorded grating. The evolution of the recording process is determined by monitoring the temporal evolution of the first diffraction order of He-Ne beam, with a detection system coupled to a computer.

The power of the Ar recording beams was $P \approx 14.5 \text{ mW}$ and the power of the He-Ne beam was 0.5 mW . The Q parameter has values lower than 0.05 for the investigated samples, therefore the diffraction on light-induced gratings is in Raman-Nath regime, which is experimentally confirmed by the appearance of several diffraction orders.

3.3. ABSORPTION MEASUREMENTS

In order to determine which optical parameters (refractive index and/or absorption coefficient) are modulated by the recording light and what kind of diffraction grating (phase, amplitude, mixed) is “seen” by the reading light, several absorption experiments have been carried out on both investigated samples, DNA-CTMA-Rh610 and PMMA-Rh610.

a) Temporal evolution of the films transmission when they are illuminated with a single Ar laser beam ($I = 2.4 \text{ W/cm}^2$) in order to check if light with this wavelength ($\lambda = 514.5 \text{ nm}$) modifies the absorption coefficient of the investigated samples. The temporal dependence of transmitted power through DNA-CTMA-Rh610 and PMMA-Rh610 films is shown in Fig. 2.

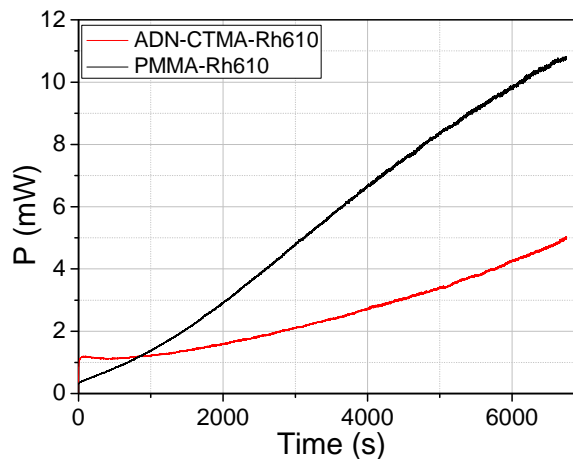


Fig. 2 – The dependence of the power transmitted through thin films of DNA–CTMA–Rh610 (red) and PMMA-Rh610 (black) at $\lambda = 514.5 \text{ nm}$.

The experimental data reveal the fact that in both samples the light induces a change of the absorption coefficient. Consequently, when two Ar laser beams are

interfering in these samples, the recorded gratings have an amplitude component given by the periodic modulation of the transmission. The increase of the transmission can be attributed to photo-degradation of Rh610 dye. The process is slower in DNA-CTMA-Rh610 than in PMMA-Rh610, suggesting that the Rh610 molecules are better protected from photo-degradation in DNA-CTMA matrix than in PMMA. This aspect is important for photonic applications of compounds containing Rh610 dye.

b) Temporal evolution of the films transmission when they are illuminated with the He-Ne probe beam alone in order to check if light with this wavelength ($\lambda = 632.8$ nm) modifies the absorption coefficient of the investigated films. The temporal dependence of He-Ne transmitted power through DNA-CTMA-Rh610 and PMMA-Rh610 films is shown in Fig. 3a. No change of the transmitted power through samples appeared during the time interval (1000 s) of the experiment, so He-Ne laser does not induce any absorption changes in our samples.

c) Temporal evolution of the films transmission at He-Ne laser wavelength when they are illuminated with a single Ar laser beam in order to check if the probe beam “sees” the change of the absorption induced by the recording beam. The temporal dependence of He-Ne transmitted power through DNA-CTMA-Rh610 and PMMA-Rh610 films illuminated with the Ar laser beam is shown in Fig. 3b. No change of the He-Ne transmitted power through samples occurred during the time interval (1000 s) of the experiment, so He-Ne laser does not “see” the absorption changes induced in our samples by the Ar laser beam.

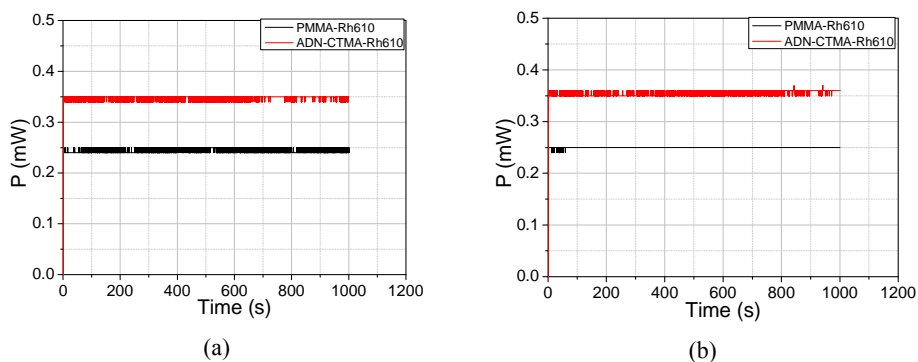


Fig. 3 – The transmitted power of He-Ne laser through thin films of DNA-CTMA-Rh610 (red) and PMMA-Rh610 (black) when the samples are illuminated with the He-Ne beam alone (a) and in the presence of the Ar laser beam (b).

In conclusion, when the two recording Ar beams interfere in our samples, the induced amplitude grating do not contribute to the diffraction of the probe He-Ne laser beam, which can be attributed to phase grating only.

3.4. TEMPORAL EVOLUTION OF THE GRATING RECORDING

The diffraction gratings have been recorded using two Ar laser beams of approximately equal intensities, $I \approx 0.6 \text{ W/cm}^2$. The recording process was studied by monitoring the temporal evolution of the diffraction efficiency of the He-Ne probe laser beam. The diffraction efficiency was fit with simple exponential relations that describe the evolution of the phase modulation:

$$\Delta\Phi(t) = \Delta\Phi_{st} \cdot [1 - \exp(-t/\tau)], \quad (9)$$

where $\Delta\Phi_{st}$ is the phase modulation in the steady state and τ is the time constant of the process.

A good fit of the experimental curves was obtained only when we considered the sum of three exponential functions of the form:

$$\Delta\Phi(t) = \sum_{i=1}^3 \Delta\Phi_{i,st} \cdot [1 - \exp(-t/\tau_i)], \quad (10)$$

with different constants, τ_i , which indicate the existence of three phase modulation mechanisms. In the steady state, the overall phase modulation is

$$\Delta\Phi_{st} = \Delta\Phi_{1,st} + \Delta\Phi_{2,st} + \Delta\Phi_{3,st}.$$

The temporal evolution of the diffraction efficiency and the fit of experimental data for the investigated samples are shown in Fig. 4.

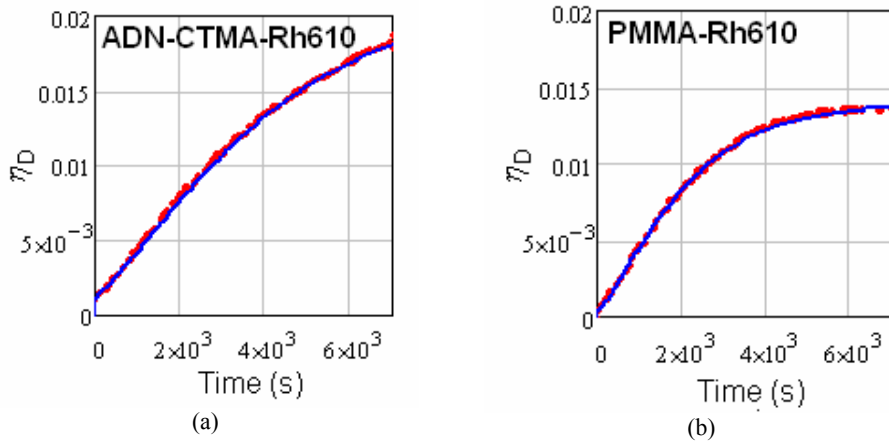


Fig. 4 – Temporal evolution of the diffraction efficiency of the gratings induced in DNA-CTMA-Rh610 (a) and PMMA-Rh610 (b) films (red: experimental data; blue: theoretical fit).

In the investigated samples, the values of τ_i and $\Delta\Phi_{i,st}$ determined from the fit of the experimental diffraction efficiency with exponential functions are shown in

the Table 1. In this table is shown also the diffraction efficiency η_D at the end of the experiment.

Table 1

The parameters of the exponential fit functions

Sample	τ_1 (s)	$\Delta\Phi_{1,ss}$	τ_2 (s)	$\Delta\Phi_{2,ss}$	τ_3 (s)	$\Delta\Phi_{3,ss}$	η_D (%)
DNA-CTMA-Rh610	0.3	0.063	80	0.005	3150	0.228	1.8
PMMA-Rh610	0.35	0.033	250	0.012	1600	0.194	1.3

The temporal evolution of the diffraction efficiency revealed a slow recording of the phase gratings induced by Ar laser in both investigated samples. The parameters of the grating evolution (values of the time constants and of the steady state phase modulations) are different in these samples, as can be seen in the Table 1. The grating evolves faster to steady state in PMMA-Rh610 than in DNA-CTMA-Rh610, the diffraction efficiency of the grating recorded in PMMA-Rh610 reaching $\eta_D = 1.3\%$ in the steady state. In DNA-CTMA-Rh610 the diffraction efficiency of the recorded grating continued to increase to the value $\eta_D = 1.8\%$ at the end of the experiment, even if the steady state was not reached until that moment.

4. CONCLUSIONS

Thin diffraction gratings have been recorded in DNA-CTMA-Rh610 and, for comparison, in PMMA-Rh610 films by interference of two Ar laser beams at 514.5 nm wavelength.

Several absorption experiments have been carried out in these samples in order to determine which optical parameters are modulated by the recording light and which of the recorded gratings are “seen” by the reading light beam. At 514.5 nm recording wavelength, the gratings induced in the investigated samples have phase and amplitude components, but only the phase grating is probed by the He-Ne beam (632.8 nm wavelength). The absorption experiments revealed also a slower photo-degradation of Rh610 dye in DNA-CTMA matrix than in PMMA.

The temporal evolution of the recording process has been investigated by monitoring the diffraction efficiency of the grating probed by a He-Ne laser beam (632.8 nm wavelength). The phase change during the grating recording was modeled in the frame of the Raman-Nath diffraction theory and it was fit with a sum of exponential functions of which parameters have been determined.

These results are important for applications in photonics of DNA-CTMA-Rh610 complex.

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