Theoretical characterization of azobenzene containing photoanisotropic materials, with special attention to polarization holography

Results of the PhD thesis

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Introduction

I performed the work described in this thesis at the Department of Atomic Physics of Budapest University of Technology and Economics on a student grant provided by Optilink Rt. The topic is connected to the development of a holographic memory card read and write system in a collaboration between the above mentioned department and firm. In this system according to the plans, the storage material will be an azobenzene containing side-chain polyester. The development of the most appropriate material for the holographic data storage is going on in RISØ National Laboratory in Denmark. My task was the modelling, examination of the response of the materials induced by light and of the effect of photoanisotropy, which is intended to be applied for data storage.

The knowledge of the response of the material on the effect of light, of the processes in the background, of the deeper interdependencies is essential for two reasons (if we see only the practical points). First it may be necessary during the design of the holographic system. Second it can provide a base for development of materials with better data storage properties. (Of course, this can be also said in case of other applications.) In the literature dealing with azobenzene containing materials we can find mainly experimental results, which can be used for the solution of the above mentioned problems, but they cannot substitute the proper theoretical interdependencies.

From viewpoint of the application it is especially essential how the material response influences the parameters of the holograms,

ization holography; experiments and theoretical modeling" (16-19 May 2002, Budapest.), poster on the *Fourth Annual Meeting of the COST Action P2* conference,.

[25] Á. Kerekes, Sz. Sajti, E. Lőrincz, S. Hvilsted and P.S. Ramanujam, *„Dynamic behaviour of azobenzene polyester used for holographic data storage"*. in Eds.: Matthias Wuttig, Lambertus Hesselink and Herman J. Borg: *Applications of Ferromagnetic and Optical Materials, Storage and Magnetoelectronics,* **674** *MRS Proceedings*, 2001, v3.4, MRS Spring *http://www.mrs.org/publications/epubs/proceedings/spring2001/v/.*

[26] Á. Kerekes, Sz. Sajti, E. Lőrincz, S. Hvilsted and P.S. Ramanujam, *„Rewritable azobenzene polyesters for polarization holographic data storage"*. in Eds.: Tung H. Jeong and Werner K. Sobotka: *Holography 2000,* **4149** *Proc. of SPIE*, 2000.

[27] E. Lőrincz, G. Szarvas, P. Koppa, F. Ujhelyi, G. Erdei, Sz. Mike, A. Sütő, P. Várhegyi, Sz. Sajti, Á. Kerekes and P.S. Ramanujam, *„Different solutions of high density holographic data storage"*. invited talk on the „Kick Off Meeting of the COST Action P8": *Materials and Systems for Optical Data Storage and Processing* conference, 24-25 June 2002, Berlin.

which are important in data storage. These are: achievable diffraction efficiency, writing speed, erasibility; besides these other properties of the material can also be interesting, e.g. the long time stability of the changes induced in the material (thus the holograms and data), and so on.

1 Background

Our knowledge about changes and phenomena in materials arising on the effect of light are still continuously growing. In recent years the phenomena connected with the reorientational ordering of the molecules on the effect of light were studied by many researchers. Such a group of phenomena is known as photoanisotropy, which can be photoinduced dichroism, birefringence or the anisotropic change arising in any other macroscopic property of the material. The photoanisotropy was observed at the first time by Fritz Weigert in silver-halide films in 1919, and later in other materials used in photography in that period [1]. Therefore it is also used to refer to this effect as Weigert-effect.

In the last century, the effect was demonstrated in a lot of other materials, e.g. in chalcogenide glasses [2, 3], which are considered interesting between holographic materials mainly because of the phenomenon of the photo-darkening [3]; in optical fibers [4]; bacteriorhodopsin films [5]; and in azobenzene containing polymers, which are treated in this thesis. In spite of the almost one century since the discovery, we cannot say of any of the above mentioned materials that we completely know the microscopic processes in the background of this effect or their role. The common in these materials is, that the orientational order of optically anisotropic microscopic physical objects: molecule-groups,-parts changes as a consequence of interaction with polarized light. This order, since the microscopic objects are anisotropic, reveals itself in the anisotropic change of the refractive index, and absorption of the material.

Besides optical data storage [6, 7], the photoanisotropic materials have numerous other applications, here we mention the optical phase conjugation [8, 9], the optical image processing [10, 11] and the creation of optical modulators and switches [12].

Kakichashvili showed in the 70-es, that the materials showing photoanisotropy can be used for recording of holograms [13]. The holograms recorded in this way contain also information about the polarization of the object wave, besides the amplitude and phase. Kakichasvili made experiments with several kind of materials: with silver-halide films applied also in photography, with inorganic glasses and with dyes [14]. He gave an expression, which is appropriate for the characterization of induced anisotropy [15]. The essence of his considerations was, that the molecules constituting the materials showing photoanisotropy are optically anisotropic, thus – as a consequence of the interaction with polarized light – an orientational dependent energy contribution is added to the energy of the molecules. The effect of this contribution reveals itself in the distortion of the orientational distribution of the molecules, which because of the optical anisotropy of the molecules is observed by the experimentalist as an anisotropic

Publications

[20] Sz. Sajti, Á. Kerekes, M. Barabás, E. Lőrincz, S. Hvilsted and P.S. Ramanujam, „*Simulation of erasure of photoinduced anisotropy by circularly polarized light*”. Opt. Com., **194**, (2001) 435–442, http://dx.doi.org/10.1016/S0030-4018(01)01308-6.

[21] Sz. Sajti, Á. Kerekes, P.S. Ramanujam and E. Lőrincz, „*Response function for the characterization of photo-induced anisotropy in azobenzene containing polymers*”. Appl. Phys. B, **Vol.?**, (2002), http://dx.doi.org/10.1007/s00340-002-0975-8.

[22] Sz. Sajti, Á. Kerekes, E. Lőrincz and P.S. Ramanujam, „*Description of photoinduced anisotropy in azobenzene side-chain polyesters*”. E-MRS, Spring Meeting, Strasbourg, Symposium F, *Organic materials for device applications*, 18 June 2002, Accepted, it will appear in the *Synthetic Metals*.

[23] P. Várhegyi, Á. Kerekes, Sz. Sajti, F. Ujhelyi, P. Koppa, E. Lőrincz, G. Szarvas and P.S. Ramanujam, „*Saturation effect in azobenzene polymers used for polarization holography*”. Under review in Appl. Phys. B.

[24] P. Várhegyi, Á. Kerekes, Sz. Sajti, P. Koppa, E. Lőrincz, G. Szarvas, P.S. Ramanujam, S. Hvilsted and P. Richter, „*Nonlinear effect in azobenzene polymers used for polar-*

[14] Sh.D. Kakichashvili, „*Polarizational (anisotropic-vectorial) holographic recording on practical photoanisotropic materials*”. Opt. Spectrosc., **42**, (1977) 218.

[15] Sh.D. Kakichashvili, „*Regularity in photoanisotropic media*”. Opt. Spectrosc., **52**, (1982) 191.

[16] S.P. Palto, V.A. Khavrichev, S.G. Yudin, L.M. Blinov and A.A. Udal'yev, „*On a model of photoinduced optical anisotropy in Langmuir – Blodgett films: low temperature studies*”. Mol. Mat., **2**, (1992) 63–72.

[17] Z. Sekkat and M. Dumont, „*Photoinduced orientation of azo dyes in polymeric films characterization of molecular angular mobility*”. Synth. Met., **54**, (1993) 373–381.

[18] T.G. Pedersen and P.M. Johansen, „*Mean-field theory of photoinduced molecular reorientation in azobenzene liquid crystalline side-chain polymers*”. Phys. Rev. Lett., **79(13)**, (1997) 2470–2473.

[19] Thomas Garm Pedersen, Per Michael Johansen, Niels Christian Rømer Holme, P.S. Ramanujam and Søren Hvilsted, „*Theoretical model of photoinduced anisotropy in liquid-crystalline azobenzene side-chain polyesters*”. J. Opt. Soc. Am. B, **15(3)**, (1998) 1120–1129.

change of the refractive index, absorption coefficient, or other characteristic quantity of the material. Besides this he assumed, that this distorted distribution 'freezes' someway in the material, thus the induced anisotropy remains still after the cessation of the illumination. A fundamental lack of this model and the derived expression is, that it does not give account of the temporal formation, evolution of the induced anisotropy.

The other problem is, that in case of azobenzene containing polymers, which are important for us, the significant 'interaction' is the absorption, and not the 'elastic' (nondissipative) interaction between the light and the matter, which was assumed by Kakichashvili. These are such sort of materials, in which the phenomenon of the photoanisotropy is based on the photoisomerization of the molecules in the material. During the photoisomerization the conformation of the molecule changes after absorption of a photon. As these molecules are optically anisotropic, therefore in case of polarized light the probability of absorption, and thus of the isomerization depends on the orientation of the molecule(part). This, as the conformational change is accompanied by the change of the orientation, leads to the distortion of the orientational distribution of the molecules, which because the anisotropy of the molecules manifests itself in the anisotropic change of the refractive index, of the absorption of the material.

For the description of the anisotropy showed by these materials are used the rate-equation approaches, which can be found in the literature [16–19]. These are based on the principle, that for description of temporal evolution of the anisotropy (birefringence, dichroism) is sufficient to know the temporal evolution of the orientational distribution of the molecules, and the proper microscopic quantities (polarizibility, absorption cross section), which do not change. Although this approach is more general, and in case of the materials important for us stands nearer to the reality, in polarization holography is still applied the expression derived by Kakichashvili, for the following reasons:

– the rate-equations, which can be found in the literature, describe only the effect of linearly polarized light,
– the rate-equations have only numerical solutions, and because of their complexity exact analytical solution is not expected.

According to experience, the expression derived by Kakichashvili – in spite of its defects – gives back properly the 'beautiful' properties of the polarization holography. After these the question arises, why is that so, and at all which are the conditions that allow the application of the expression derived by Kakichasvili.

2 Results

Essentially in this thesis, I attempted to give answer to the above mentioned questions. In order to do this, I generalized the available models, and I checked the merit of the extended models by comparison with experimental results. I found that the results, which can be gained by means of the two methods showed in this thesis, are usable for estimation in circumstances important for us. Besides this it is apparent as well from the examinations that there are still numerous open questions, which could be answered

tide oligomers for holographic data storage". Nature, **383**, (1996) 505–508.

[8] A.N. Simonov, A.V. Lavrichev, V.P. Shibaev and A.I. Stakhanov, *„High-quality correction of wavefront distortions using low-power phase conjugation in azo-dye containing LC polymers"*. Opt. Com., **197**, (2001) 175–185.

[9] A.A.R. Awangku Yusof, S.V. O'Leary and G.R. Mitchell, *„Temperature-tuned vector phase conjugation in azobenzene dye impregnated polymer films"*. Opt. Com., **169**, (1999) 333–340.

[10] M.Y. Shih, A. Shishido and I.C. Khoo, *„All-optical image processing by means of a photosensitive nonlinear liquid-crystal film: edge enhancement and image addition-subtraction"*. Opt. Lett., **26(15)**, (2001) 1140–1142.

[11] Tizhi Huang and Kelvin Wagner, *„Photoanisotropic incoherent to coherent conversion using five wave mixing". Devices for optical processing* 1562, SPIE, 1991, 44–54.

[12] A.V. Tomov and A.I. Voitenkov, *„All-optical modulation in azo-dye-doped polymer waveguides"*. Opt. Com., **174**, (2000) 133–137.

[13] Sh.D. Kakichashvili, *„Method for phase polarization recording of holograms"*. Sov. J. Quant. Electron., **4**, (1974) 795.

References

[1] Fritz Weigert, „*Über einen neuen Effekt der Strahlung in lichtempfindlichen Schichten*". Ver. d. D. Phys. Ges., **21**, (1919) 479–491, 615–622, 623–631.

[2] K. Tanaka, K. Ishida and N. Yoshida, „*Mechanism of photoinduced anisotropy in chalcogenide glasses*". Phys. Rev. B, **54(13)**, (1996) 9190–9195.

[3] P. Krecmer, A. Sklenar, M. Vlcek and S.R. Elliott, „*Photoinduced effect in glassy crystalline* As_4Se_3*: Negative photoinduced anisotropy*". Phys. Rev. B, **63**, (2001) 104201.

[4] D.C. Psaila, F. Quellette and C. Martijn de Sterke, „*Characterization of photoinduced birefringence change in optical fiber rocking filters*". Appl. Phys. Lett., **68(7)**, (1996) 900–902.

[5] E.Ya. Korchemskaya, D.A. Stepanchikov and T.V. Dyukova, „*Photoinduced anisotropy in chemically-modified films of bacteriorhodopsin and its genetic mutants*". Opt. Mat., **14**, (2000) 185–191.

[6] Søren Hvilsted, Fulvio Andruzzi, Christian Kulinna, Heinz W. Siesler and P.S. Ramanujam, „*Novel side-chain liquid crystalline polyester architecture for reversible optical storage*". Macromolecules, **28(7)**, (1995) 2172–2183.

[7] Rolf H. Berg, Søren Hvilsted and P.S. Ramanujam, „*Pep-*

only by further theoretical and experimental investigations.

I summarized my results in the following points:

1.) I extended the model of Ref. [19] based on rate-equations, which describes only the effect of linearly polarized light. The extended model is appropriate for the description of the effect of lightsources with arbitrary polarization [20] and coherence properties [20, 21]. I checked the model by means of comparison with experimental results. I showed that the relaxation approximation assumed in the model is not appropriate for the description of the "dark-relaxation' of the induced anisotropy [20].

2.) For the characterization of polarization holograms, a phenomenological formula derived by Kakichashvili was applied, whose applicability was strongly constrained by the fact that it does not count with the temporal evolution of the photoinduced anisotropy. I derived an expression from the extended rate-equations which characterizes the photoanisotropic response of the material [21]. This expression (I call it response function) contains the above mentioned Kakichashvili's expression, thus explains its success experienced in polarization holography. Further the response function depends also on time, and it takes into account the saturation of the induced anisotropy with time and intensity.

3.) The material constants playing role in the response function arise automatically in the course of derivation, thus they can be also calculated [21]. I calculated them for a group of materials as a function of wavelength. The wavelength dependency of the constants gained this way agrees qualitatively well with the experimental experiences. The theoretically calculated values of these constants are appropriate for further estimations [21].

4.) I also investigated the change of the response function in case of initially not isotropic material. I showed that in case we calculate with the response function of initially isotropic materials, the error of the calculation is determined by the initial order parameters S_2, S_4 [21].

5.) I investigated how the numerical solution of rate-equations and the derived response function can be used for the characterization of a special case of the polarization holography. I found that the agreement between the results gained by the two methods are acceptable in the examined cases [21, 22].

6.) I showed that the dependency of the diffraction efficiency on the intensity ratio of reference and object beams cannot be interpreted by means of the Kakichashvili's expression, but it can be done by the expression derived by me, which takes into account the saturation of the anisotropy [21]. This has a significance especially in Fourier-holography [23].

7.) I investigated the limits of solutions presented in this thesis. I showed that the response function is not appropriate – and neither the Kakichashvili's expression – for the description of erasure and multiplexing because of the approximations

applied during derivation. To solve these problems we need a method based on the solution of the extended rate-equations [22].