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Local Electric Field Effects and Second Harmonic Generation in Langmuir-Blodgett Films

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LOCAL ELECTRIC FIELD EFFECTS AND SECOND HARMONIC GENERATION IN LANGMUIR-BLODGETT FILMS

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Abstract Local electric field of light waves in Langmuir-Blodgett film is calculated, and its effect on optical second harmonic generation (SHG) is estimated. Strong dependence of SHG intensity on the film thickness is explained.

INTRODUCTION

Quick development of Langmuir-Blodgett technique and plane wave guides devices gave rise to numerous experimental investigations of linear and nonlinear optical properties of these media, and they show promising characteristics (both efficiency and reliability) and clear perspectives for further improving. It is clear that long organic molecules of LB films may be modified to increase their nonlinear polarizabilities β up to very high values, and well ordered structure of the films provides them with high total nonlinear susceptibility χ. It would be useful for such investigations to connect molecular β, film structure and the total χ, as it is the case for bulk molecular crystals.[1-3] For this reason here we try to simulate local electric field in the LB film structure and the effect of its distribution on the film nonlinear susceptibility.

THE MODEL

As usual we consider the connection of macroscopic χ and local β in the form:

$$\chi_{ijk} = \frac{1}{V} f_{ii'}^{\mu} \beta_{i'j'k'} f_{j'j}^{\mu} f_{k'k}^{\mu} \qquad (1).$$

Here and below summation over all repeated indices is done, and $f_{ii'}^{\mu}$ is a local field tensor, connecting Maxwell macroscopic field $\mathbf{E}$ in the film and local field $\mathbf{F}^{\mu}$ at the μ-th molecule:

$$F_i^{\mu} = f_{ii'}^{\mu} E_{i'} \qquad (2).$$

The structure of this tensor is to be very special for LB films due to:

i) strongly anisotropic molecules of the film;

ii) strongly anisotropic molecular packing of the film;

iii) limited and rather small size of the film in the film normal direction;

iv) molecular length being of the same order as the film thickness.

All these factors are to be taken into account for local field simulation, and usual isotropic approximation seems to be too rough in this case.

Problems i-ii may be solved in the same way as it has been done in usual molecular crystals[2-4], i.e. by direct summation of molecular dipoles fields over film structure, and using Ewald approach for better convergence. In the framework of this approach it's easy to take into account limited film thickness as well. As for molecular length, it means that point dipole approximation can't be used for LB molecules. Multipole expansions seem not good as well; molecular length being of the same order (if not more) as intermolecular distances would result in a very poor convergence of multipole series. So we've preferred to divide molecules under simulation into 2 - 3 'scattering centers' (hard core and flexible tails) and calculate lattice sums for them.[3] But in this case we have to know

fragment's polarizabilities; besides it complicates summation considerably. To simplify this task, we use mean molecular lattice sums (meant over fragments of the given molecule, weighted with fragment's polarizabilities).[3] As in this case only relative fragment's polarizabilities are actually used, we've estimated them using additive scheme.

We based our model parameters on the data of papers[5-6] where both linear and nonlinear optical properties of LB films had been measured quantitatively together with structural data. The same optically nonlinear molecules have been taken for simulation:

$$H_{25}C_{12}- NCH_3- C_6H_4- N = N\ C_6H_3NO_2- COOH \qquad (3),$$

$$HOOC - C_2H_4- NCH_3- C_6H_4- N = N - C_6H_4- C_{17}H_{35} \qquad (4),$$

$$H_{25}C_{12}- C_6H_3NO_2- N = N - C_6H_4- NCH_3- COOH \qquad (5),$$

and arachidic acid molecule as a passive buffer. Molecular hyperpolarizabilities β have been estimated using the same additive scheme and fragment's data.[7] A single LB layer has been considered as square lattice of uniaxial molecules, and local field tensor (2) at the molecules as well as macroscopic nonlinear susceptibility χ (1) have been simulated for different structures (uniform Z stack of active layers, Y stack of alternating active layers, single active layer on passive Y stack of buffer molecules) as a function of the film thickness N (see Table 1 for model parameters).

TABLE 1 Model parameters.

Molecule	Layer thickness(Å)	Lattice parameter(Å)	$\beta(10^{-40}$, SI units)
1	32.0	6.0	929
2	42.0	6.1	1541
3	32.0	5.9	929

RESULTS AND DISCUSSION

Obtained values of macroscopic χ agree enough good with experimental ones, that proves the correctness of

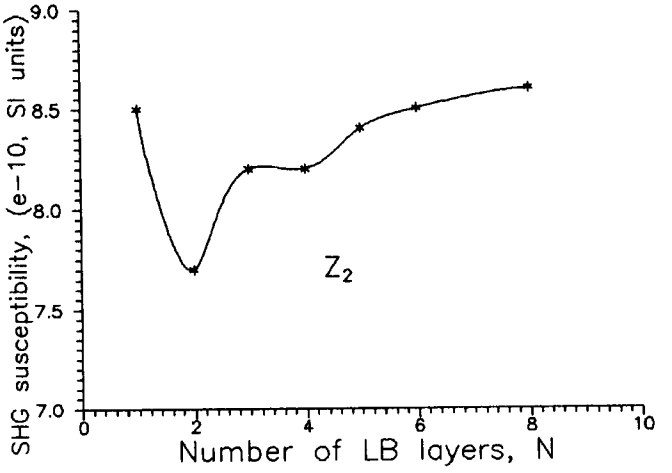

FIGURE 1 Dependence of nonlinear susceptibility of Z stack of molecules (5) on the layers number N.

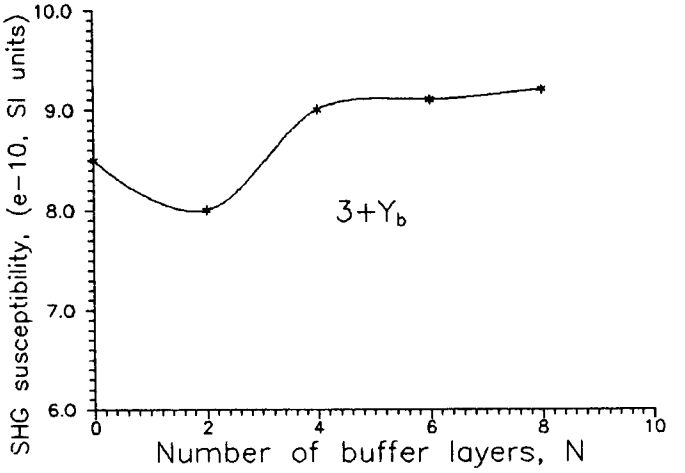

FIGURE 2 Dependence of nonlinear susceptibility of single layer of molecules (5) placed on Y stack of buffer molecules, on the stack thickness N.

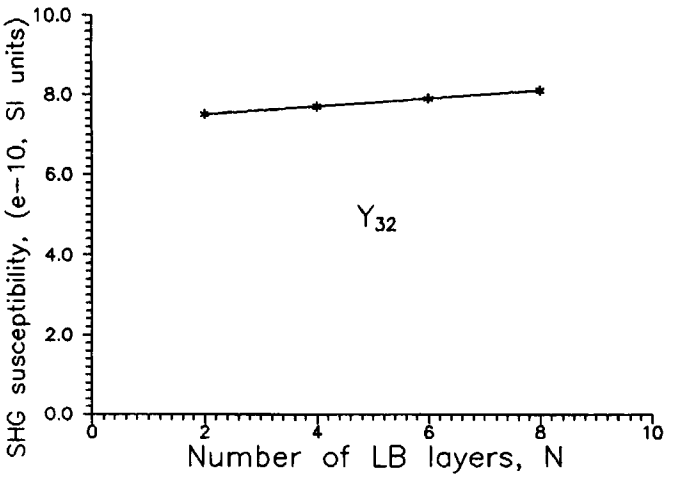

FIGURE 3 Dependence of nonlinear susceptibility of alternating Y stack of molecules (5) and (4) on the layers number N.

performed calculations. The most typical of obtained dependencies are shown in Fig. 1-3. The most drastic dependence $\chi = \chi(N)$ has been obtained for Z stacks - after quick decrease at first two - three layers it shows typical odd-even alterations and converges to bulk nonlinear susceptibility at $N \approx 20$, where contribution of surface layers into total χ becomes negligibly small. Such alterations may result in SHG instability in such films, if their structure is not ordered enough, as it has been observed experimentally.[5] The same though smaller effect of local field inhomogeneity has been obtained for single active layer on passive buffer stack (Fig.2).

Alternating Y stacks formed of highly nonlinear molecules show the most stable behavior (Fig.3). Their macroscopic χ appears practically independent on film thickness; its alterations were less then 10% for all simulated structures of this kind. It explains stability of experimental SHG intensity observed in these films as well.[5,6]

So proposed model gives reasonable results and may be effectively applied for local electric field simulations in strongly anisotropic LB films. It seems promising to develop it further taking into account: i)changes of molecular parameters due to intermolecular interactions; ii) orientational and structural disorder of molecular packing in LB films; iii) macroscopic field inhomogeneity. Such model is in progress now.

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REFERENCES

1. N.Bloembergen, Nonlinear Optics (W.A.Benjamin, Inc. New York - Amsterdam, 1965).
2. M.Hurst, R.B.Munn, J.Mol.Electron., 2, 101, (1986).
3. A.N.Botvich, V.G.Podoprigora, V.F.Shabanov, N.P.Shestakov, A.N.Vtyurin, Phys.stat.sol., b120, 491, (1983).
4. R.B.Munn, T.Luty, Chem.Phys., 37, 413, (1979).
5. I.Ledoux, D.Josse, J.Zyss, T.McLeen, P.F.Gordon, R.A.Hann, S.Allen, J.chim.phys., 85, 1085, (1988).
6. I.Ledoux, D.Josse, P.Flemaux, J.-P. Pid, G.Post, J.Zyss, T.McLeen, R.A.Hann, P.F.Gordon, S.Allen, Thin Solid Lilms, 160, 217, (1988).
7. Nonlinear Optical Properties of Organic Molecules and Crystals, ed.by D.S.Chemla, j.Zyss (Academic Press, Inc., Orlando etc., 1987), Suppl.2.
8. L.G.Koreneva, V.F.Zolin, B.D.Davydov. Nonlinear Optics of Molecular Crystals (Nauka Publishers, Moscow, 1985).