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on surface nonlinear optics

Second-harmonic generation on reflection from a monomolecular Langmuir layer

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The generation of the second harmonic on reflection of light from a monomolecular Langmuir layer (MLL) is observed for the first time. The component of the quadratic-susceptibility tensor $\chi^{(2)}_{yyy} = 4.2\times 10^{-8}$ esu is measured for an MLL of nitro-octadecylazobenzene.

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Monomolecular Langmuir layers (MLL) are of interest for optoelectronics, since they permit obtaining thin-film structures with fixed optical,[1] wave guide-optical,[2–4] and pyroelectrical[5] properties.

1. In this work, the nonlinear optical properties of MLL of 4-nitro-4′-*N*-octadecy-

lazobenzene (NAB) molecules, deposited on a substrate consisting of fused quartz, is investigated for the first time. NAB, whose structural formula is $O_2N\langle\ \ \rangle N=N\langle\ \ \rangle N-HC_{18}H_{37}$, belongs to a wide class of chemical compounds whose molecules contain a conjugate donor-acceptor system and have large nonlinear optical polarizabilities.[6,7] However, crystals of such compounds often have a center of inversion and their quadratic nonlinear susceptibility $\chi^{(2)}=0$.

2. To obtain the MLL, we used an arrangement similar to that in Ref. 8. The MLL was formed on a water surface from a solution of NAB in benzene. The MLL was transferred to the substrate by drawing the latter through the interface while simultaneously compressing the section of the surface occupied by the NAB. The surface density of NAB molecules calculated from the transfer coeffieient constituted $\sim 3\times 10^{14}$ cm^{-2}.

Generation of the second harmonic (SH) was observed with reflection from the MLL of YAG-Nd^{3+} laser radiation with wavelength $\lambda=1060$ nm, repetition frequency 12 H, and pulse duration $\tau\approx 15$ ns with 0.5–5 mJ per pulse. The SH radiation with $\lambda=530$ nm was collected by a system of lenses on the input slit of a DFS-24 monochromator. At the output of the monochromator the SH intensity was measured by a detection system consisting of a FÉU-79 and an amplitude-digital converter. The detection system was calibrated according to the SH intensity on reflection of light from a silver surface, for which $\gamma=(I_{2\omega}/I_{\omega}^2)^{1/2}=1.3\cdot 10^{-9}$ esu,[9] where $I_{2\omega}$, I_{ω} is the SH intensity and the intensity of pumping radiation, respectively.

3. The geometry of the experiment is shown in Fig. 1. The plane of the substrate with the MLL coincides with the $Z=0$ plane and the plane of incidence of the pumping radiation coincides with the $Y=0$ plane. The angle of incidence of pumping radiation was 45°. The SH radiation was collected at an angle of 90° to the pumping direction. The pumping radiation was linearly polarized and s and p polarizations were selected. The intensity of s and p polarized SH radiation was measured for each polarization of the pumping radiation. For p-polarized incident radiation, γ is $3.2\cdot 10^{-9}$ esu and $2.5\cdot 10^{-9}$ esu for p and s polarized SH radiation, respectively. For s polarized

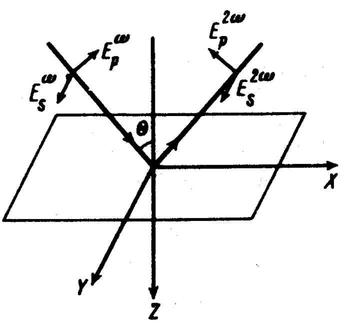

FIG. 1. Geometry of the experiment on generating second-harmonic radiation by reflecting light from a monomolecular Langmuir layer. $Z=0$ is the plane of the Langmuir film, $Y=0$ is the plane of incidence of the pumping radiation, and $\theta=45°$ is the angle of incidence of the pumping radiation. For s polarization the **E** vector is perpendicular to the plane of incidence and for p polarization the **E** vector lies in the plane of incidence.

pumping radiation with p and s polarized SH radiation, γ is 0.9×10^{-9} esu, and 3.1×10^{-9} esu, respectively.

The films obtained by the Langmuir-Blodgett method consist of microcrystallites, each of which has molecules oriented parallel to each other at some angle relative to the normal to the plane of the film. It was assumed in Ref. 10 that due to the isotropic distribution of the orientation of microcrystallites relative to the normal, the film has $C_{\infty v}$ symmetry with the infinite-order axis oriented along the normal. For MLL of such symmetry the s polarized component of SH radiation is missing for p and s polarization of the pumping radiation. The appreciable intensity of polarized SH radiation leads to the conclusion that $C_{\infty v}$ symmetry is missing in the MLL studied. The predominant orientation of the microcrystallites is apparently related to the drawing orientation or the orientation of compression of the monolayer when it is formed.

The measurements of γ permit estimating the product of the quadratic-susceptibility tensor $\chi^{(2)}_{yyy}$ by the thickness of the Langmuir layer d: $-\chi^{(2)}_{yyy}d\approx 8.4\times10^{-15}$ esu. For our MLL, $d=20$–30 Å and for the quadratic susceptibility we have $\chi^{(2)}_{yyy}\approx(2.8-4.2)\times10^{-8}$ esu. The quadratic susceptibility of MLL consisting of NAB molecules has the same order of magnitude as in lithium niobate crystals.

Thus we have demonstrated the possibility of observing second-order nonlinear optical effects in ordered monomolecular layers condensed on a solid substrate by the Langmuir-Blodgett method.

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