PHYSICAL REVIEW B VOLUME 41, NUMBER 7 1 MARCH 1990

Anisotropic second-order nonlinearities of organic monolayers

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(Received 12 September 1989)

Monolayers prepared from hemicyanine chromophores of high second-order nonlinearity ($\beta = 1.3 \times 10^{-26}$ esu at resonance) have been used to study anisotropies of the concomitant $\chi^{(2)}$-susceptibility tensor. All components of this third-rank tensor have been determined by Fourier analysis of the anisotropic coverage density $N_s(\phi)$ with respect to the angle of rotation about surface normal. Depending on the preparation both C_s and C_{2v} symmetry could be identified.

Second-harmonic generation (SHG) with its high intrinsic surface specificity has been developed into a powerful tool for the analysis of surface layers and adsorbates between two centrosymmetric media.[1–5] Surface symmetry analysis in terms of the determination of a rotational anisotropy around the surface normal has been so far restricted to the identification of threefold and fourfold axes of (bulk-) centrosymmetric semiconductors and metals.[3,6–9] Molecular monolayers prepared from organic dyes usually exhibit rotational isotropy around the surface normal,[1,10,11] although deviations from isotropy have been documented in the literature.[12] In principle, well organized organic monolayers with thicknesses of 1–2 nm and hence orders of magnitude smaller than the wavelength of light are a perfect realization of the idea of a "polarization sheet"[13] responsible for the emission of SH radiation from the surface location.[14] With the now available dyes of a nonlinear second-order hyperpolarizability $\beta \geq 10^{-27}$ esu,[15] it should be possible to determine subtle details of the $\chi^{(2)}$ surface tensor exceeding the information derived from isotropic averaging. It is the purpose of this paper to demonstrate that it is possible to determine all components of the $\chi^{(2)}$ tensor of an anisotropic organic monolayer by polarization-dependent excitation and detection and rotation of the samples about the surface normal. Such rotation experiments allow the determination of the various components of a second-order tensor. The tensor components have been split into sums of the respective contributions, representing onefold, twofold, threefold, and ∞-fold or isotropic symmetry, which could be conveniently determined with appropriate precision by analysis of the rotation pattern. Optical heterodyning via injection of an external anisotropic signal produced by surface reflection from a gold (111) face served as an additional test for the proper sign and magnitude of the experimentally determined tensor components.[16]

The nonlinear polarization responsible for the SH response of a monolayer can be expressed by

$$P_i(2\omega) = \chi_{ijk} : E_j(\omega) E_k(\omega) \ ,$$

where i,j,k denote vector components with respect to the x-y-z coordinate system shown in the inset of Fig. 1 and the sum convention rule applies. The fundamental field is $E(\omega)$ and $\chi^{(2)} = \{\chi_{ijk}(2\omega)\}$ denotes the third-rank susceptibility tensor, which reflects the symmetry of the monolayer. Let us consider a distribution of cylinder-symmetric molecules on a plain surface. Rather than in the most general case of triclinic (C_1) symmetry and 18 nonvanishing components,[17] such an arrangement will exhibit monoclinic symmetry C_s with inclusion of one mirror plane. According to the considerations of Ref. 18 an ensemble of rodlike molecules with one dominant hyperpolarizability component along its symmetry axis can be described in terms of a $\chi^{(2)}$ tensor of only six independent components instead of ten components for the general C_s configuration:

$$\begin{aligned} &\chi_{xxx}, \chi_{xyy} = \chi_{yxy}, \chi_{xzz} = \chi_{zxz} \ , \\ &\chi_{zzz}, \chi_{zxx} = \chi_{xxz}, \chi_{zyy} = \chi_{yyz} \ . \end{aligned} \tag{1}$$

In standard orientation these components form ($m \perp y$ axis) in contracted notation the following tensor:

$$\begin{array}{cccccc} xx & yy & zz & yz & xz & xy \\ \chi_{xxx} & \chi_{xyy} & \chi_{xzz} & & \chi_{zxx} & \\ & & & \chi_{zyy} & & \chi_{xyy} \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & & \chi_{xzz} & \end{array} \ . \tag{1a}$$

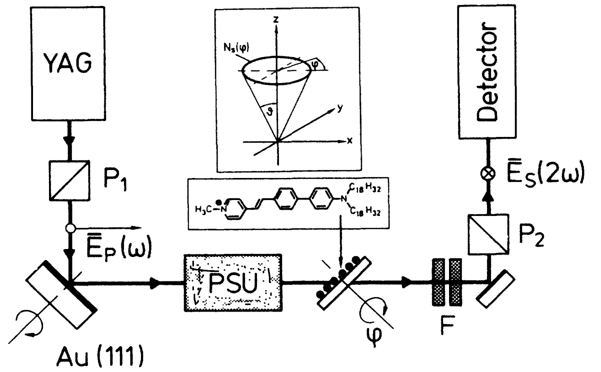

FIG. 1. Experimental layout of optical heterodyning experiment with anisotropic hemicyanine monolayer. Inset shows chemical structure and coordinate system used for Fourier analysis of coverage density $N_s(\varphi)$.

It should be noted that the reduction of the number of independent components from ten to six for C_s symmetry is *formally* equivalent to the result obtained by application of Kleinman's conjecture,[19] in which indices are cyclically permutable for nonresonant excitation. However, in this case, the reduction of the number of independent components is a fundamental symmetry property of the susceptibility tensor and therefore applies in all spectral ranges of interest.

In the analysis of the experiments to be described in the following we have studied several assumptions concerning the tilt angle with respect to the surface normal and its distribution. It turned out that the rotation patterns could only be described without any severe contradictions if we assumed a constant molecular tilt angle of narrow distribution around its average value. This is basically the same assumption that is used for isotropic layers, where an average tilt angle θ is derived from the ratio

$$\tan^2\theta=(\chi_{zxx}+\chi_{zyy})/\chi_{zzz}$$

as discussed in detail in Ref. 11. Assuming that the nonlinear molecules form such a well-defined cone-shaped distribution, anisotropic behavior can be introduced by an anisotropic distribution of the coverage density $N_s(\phi)$ along the cone circumference as shown in Fig. 1. The components of tensor (1a) can be calculated by evaluation of the respective Fourier integrals with

$$N_s(\phi)=\frac{1}{2\pi}\sum_{m=0}^{m=3}N_m\cos(m\phi)\ , \tag{2}$$

and the total coverage density $N_s=N_0$, which is the density of the isotropic distribution N_∞. Separating the incoming electric fields into their components according to the coordinate system of Fig. 1 yields the following expressions for the components of tensor (1a):

$$\chi_{xxx}=\beta/8\sin^3\theta(3N_1+N_3)\ \ \{N_1\cos\phi;+N_3\cos3\phi\}\ ,$$

$$\chi_{xyy}=\beta/8\sin^3\theta(N_1-N_3)\ \ \{N_1\cos\phi;-N_3\cos3\phi\}\ ,$$

$$\chi_{xzz}=\beta/2\sin\theta\cos^2\theta N_1\ \ \{N_1\cos\phi\}\ ,$$

$$\chi_{zxx}=\beta/4\cos\theta\sin^2\theta(2N_0+N_2)\ \ \{N_0;+N_2\cos2\phi\}\ ,$$

$$\chi_{zyy}=\beta/4\cos\theta\sin^2\theta(2N_0-N_2)\ \ \{N_0;-N_2\cos2\phi\}\ ,$$

$$\chi_{zzz}=\beta\cos^3\theta N_0\ \ \{N_0\}\ .$$

The expressions in curly braces denote the expected amplitudes upon sample rotation about the z axis. The angle ϕ is the azimuthal angle with $\phi=0$ the x axis according to Fig. 1. In the absence of anisotropies ($N_1=N_2=N_3=0$) the components reduce to the expressions for isotropic distributions,[1,10,11] in particular $\chi_{zxx}=\chi_{zyy}\neq\chi_{zzz}$, and all other elements vanish.

The basic experimental idea was to achieve directional control of a high second-order nonlinearity by spreading a monolayer onto an anisotropic substrate. The substrate consisted of freshly cleaved gypsum single crystals of monoclinic C_2 symmetry.[20] All experimental results will be discussed in terms of a single, dominant component $\alpha_{zzz}=\beta$ of the molecular hyperpolarizability tensor $\alpha^{(2)}$, with $\beta=1.5\times10^{-27}$ esu at 1064 nm and a resonance value as high as 1.3×10^{-26} esu at 840 nm. A Nd-YAG laser producing 3-ns pulses at 1064 nm of a pulse energy of 12 mJ at a 10-Hz repetition rate was used, and its radiation focused to a spot size of 0.01 cm^2. Optical heterodyning experiments served to calibrate the tensor components with respect to sign and magnitude. The advantages of this technique, phase-controlled superposition of two nonlinear optical signals of individually adjustable height, have recently been discussed in detail elsewhere.[16] Figure 1 shows the actual experimental equipment used. Typically up to 60 mJ were necessary to produce an appropriate 2ω signal at the gold surface and to generate enough SH radiation at the position of the anisotropic films after passage through a phase-sifting unit (PSU in Fig. 1). Best results as to phase measurements[16,21] have been obtained with a gas cell of 10-cm length and adjustable N_2 pressure. The SH signal from the gold (111) face was preferred to other 2ω sources such as silicon faces or another dye monolayer because of its high reflectivity for the fundamental and because of the convenience in adjusting the amplitude and phase of this 2ω-reference signal by simple rotation of the gold crystal around its surface normal. The polarizer P_1 and P_2 determined the polarization conditions of the experiment, usually p-polarized excitation and s-polarized detection of the resulting 2ω signal.

A first experiment has been performed under these polarization conditions with a monolayer still on gypsum and a 45° angle of incidence. The optical activity of the substrate did not allow the usual polarization-dependent

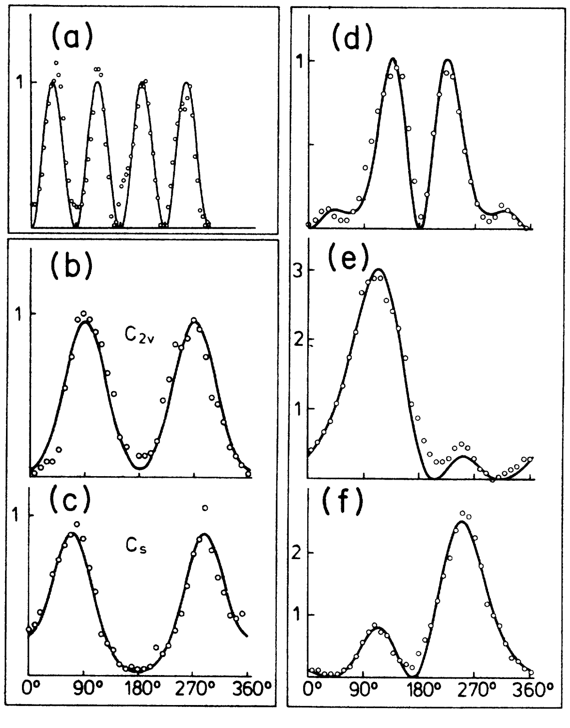

FIG. 2. Second-harmonic intensity versus rotation angle ϕ for the various experimental conditions discussed in the text.

measurements in transmission. The rotation pattern of Fig. 2(a) serves as a preliminary symmetry test of the freshly prepared samples. It demonstrates the agreement with our symmetry expectations: Instead of monoclinic C_2 symmetry the molecular orientation of the anisotropic film shows orthorhomobic C_{2v} symmetry. The rotational pattern shows perfect symmetry with respect to the y-z plane and hence the absence of any odd-symmetry axes. In fact, the ratio N_1/N_0 was less than 1% corresponding to the experimental accuracy and reproducibility from sample to sample. The pattern of Fig. 2(a) can be described with a single component of tensor (1a), $\chi_{yxz} \propto \sin 2\phi$, with the x and y axes denoting the two symmetry axes of the orthorhombic class C_{2v}. Apparently the molecules organize only along a preferred direction of the crystalline substrate and hence show higher symmetry than gypsum. Monolayer transfer onto hydrophobic quartz substrates usually resulted in reduction of the primary C_{2v} symmetry to C_s symmetry. If flotation of the film from the crystal and transfer to quartz was, however, done with great care in handling the invisible film, the original symmetry could be preserved: Figures 2(b) and 2(c) show, in comparison, a case of C_{2v} symmetry and the more frequently encountered case of C_s symmetry. The differences are small, but are, however, clearly discernible by the broadening of the intermediate minimum around $\phi = 180°$ due to additional contributions from the onefold and threefold symmetry. In fact, both χ_{xyy} and χ_{zyy} contribute to the C_s rotation pattern of Fig. 2(c), while χ_{zyy} contributes only to Fig. 2(b). Based upon these considerations, the Fourier amplitudes are $N_\infty = 1$, $N_2 = 0.73$ for the C_{2v} symmetry of Fig. 2(b), and $N_\infty = 1$, $N_1 = 0.85$, $N_2 = 0.69$, $N_3 = 0.28$ for the C_s symmetry of Fig. 2(c). The respective tilt angles θ were 45.5° and 26.1°. All susceptibility data refer to the aforementioned β value (1.5×10^{-27} esu) and a coverage density $N_s = N_0 = N_\infty = 1.2 \times 10^{14}$ cm^{-2}. To facilitate the comparisons between C_{2v} and C_s symmetry, the N_∞ values have been normalized to 1. The data $N_\infty = 1$ and $N_2 = 0.73$ indicate in the case of C_{2v} symmetry that all molecules of the monolayer participate in the isotropic distribution and that 73% also participate in the generation of the twofold symmetry axis. The contributions of the Fourier amplitudes N_1 and N_2 could be independently checked by linear, dichroic absorption measurements. In general, all preparations on gypsum crystals had a much narrower distribution around the surface normal as compared to previous work,[15] where tilt angles as high as 82° were measured. We attribute the narrow distribution to both, the influence of the primary crystalline substrate and the successful transfer onto a hydrophobic quartz surface together with the protection of the layer orientation by an overlayer of arachidic acid. The influence of the overlayer is actually threefold: It helps to stabilize the layer during the transfer process, and it shields it against environmental effects.[15] A systematic comparison of monolayers with and without (SH inactive) overlayers revealed in addition that monolayers with overlayers tend to align in a very narrow tilt-angle distribution provided the lengths of the aliphatic chains of both materials are properly matched. In the case of the sample with C_s symmetry the high degree of directionality towards the surface normal leads to a susceptibility component χ_{zzz} as high as 1.27×10^{-13} esu. It has been discussed in some detail in Ref. 20 that the orientation of a surfactant chromophore follows crystallographic axes and depends on the size of the molecules, provided that aggregation phenomena do not interfere with the orienting tendency of the anisotropic substrate. The selected hemicyanines under our experimental conditions showed no sign of aggregation. Aggregation phenomena are a severe problem at high coverage densities exceeding 2.0×10^{14} cm^{-2} and may even lead to a misinterpretation of the β values derived from susceptibility measurements. The selected hemicyanine dye has so far shown no tendency to form aggregates in contrast to other hemicyanines of different aliphatic chain lengths.[22] The absence of aggregation was additionally confirmed from the linear-optical absorption spectra prepared from each monolayer sample.

With reference to Figs. 2(d)–2(f) we would like to demonstrate the usefulness of the optical heterodyning technique. Figure 2(d) shows a rotation pattern of another sample of C_s symmetry obtained under p-polarized excitation and s-polarized detection, and hence, according to the C_s tensor (1a), no isotropic contribution is symmetry allowed. One might be tempted to explain such a pattern as C_2 symmetry in terms of a superposition of an anisotropic signal due to twofold symmetry with an isotropic background. Injection of external signals with reversed phases [Figs. 2(e) and 2(f)], however, clearly reveals the dominant contribution from the onefold symmetry. Only the tensor components χ_{yxx} and χ_{yzz} show the sign reversal at $\phi = 180°$. The measured susceptibilty components are $\chi_{yxx} = 1.8 \times 10^{-15}$ esu and $\chi_{yzz} = 25.9 \times 10^{-15}$ esu for Fig. 2(d) with no injection, and an injected, quasi-isotropic signal of magnitude $(13.5 \pm 3) \times 10^{-15}$ esu of positive phase for Fig. 2(e) and negative phase for Fig. 2(f).

We have studied the symmetry properties of a $\chi^{(2)}$ tensor of monoclinic C_s symmetry and transitions between orthorhombic C_{2v} and C_s symmetry. All isotropic and anisotropic tensor elements could be experimentally determined by sample rotation and polarization-sensitive excitation and SH detection. The sample was a monolayer prepared from organic molecules of extremely high molecular hyperpolarizability, first deposited onto an anisotropic crystalline surface and then transferred onto a hydrophobic substrate of fused quartz. We present an analysis of the anisotropic coverage density, which correlates with the observed onefold, twofold, threefold, and ∞-fold symmetry. The analysis also reduces the number of six independent elements of the C_s tensor to four new parameters: The average tilt angle θ of the molecules with respect to the surface normal and the coverage density Fourier coefficients N_1, N_2, and N_3 of the symmetry axes that can be resolved by a third-rank tensor.

The technique of directional control of a nonlinear surface layer[23] will also be useful for the enhancement of the SH-conversion efficiency. Considering a uniaxial texture, where the onefold symmetry dominates and χ_{yyy} is the only relevant susceptibility component, we expect for the situation of 45° incidence an increase in conversion efficiency by a factor of 15 as compared to an experiment with χ_{zzz} as the dominant component under properly chosen polarization conditions. In Ref. 24 a new approach for the achievement of large-scale phase matching using surface effects has been proposed. Incorporating the advantages of anisotropies may further increase the conversion efficiency of such devices that make use of surface effects, and which are, according to Ref. 24, already superior to frequency convertors made from inorganic crystals.

ACKNOWLEDGMENTS

The novel hemicyanine chromophores were synthesized with high purity by D. Dorsch, Merck/Darmstadt. G. Debuch performed the various Langmuir-Blodgett preparations with great care. We thank N. Ernsting and A. Müller for a critical reading of the manuscript and for various helpful suggestions.

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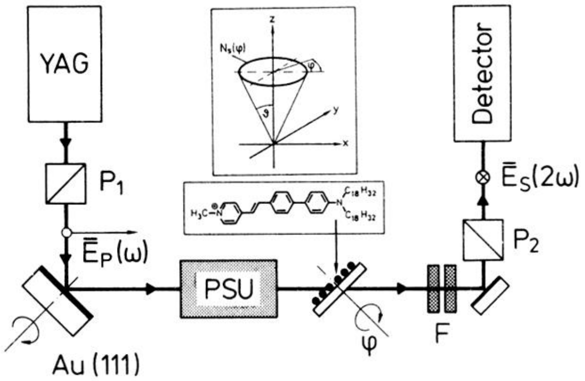

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