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ALIGNMENT OF DYE MOLECULES STUDIED THROUGH SURFACE SECOND-HARMONIC GENERATION

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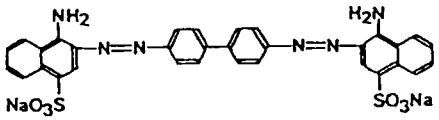
Abstract It has been found that Congo Red and its homologs can be aligned along a direction by mechanically brushing thin films of the dyes. The films were studied through polarized absorption and surface second-harmonic generation.

Molecular orientation is of paramount importance for efficient second harmonic generation (SHG). The second order hyperpolarizability vanishes in a system with an inversion symmetry. Much effort has been made to realize a crystal with a low symmetry, so that a nonlinear polarization induced on molecules adds up to a large macroscopic nonlinear polarization.[1] Orientation of molecules in a crystal lattice can be influenced by lowering the molecular symmetry by introducing substituents, including chiral groups. In some cases intermolecular hydrogen bonding can be profitably used to keep a head-to-tail arrangement in a crystal. Such approaches are termed "crystal engineering". LB and built-up films are attractive also in this context. With polymeric materials the electric "poling" technique can be also applied.

Here will be reported an unconventional means for orienting molecules: by mechanical brushing. We have found that certain dyes, Congo Red



for example, can be aligned by mechanically brushing thin films of the dyes.[2] Thin (typically 15 nm thick) films are prepared by spin-coating an aqueous solution of Congo Red onto glass plates. Optically homogeneous films are obtained. When examined under polarization microscope they exhibit no indication of crystallization and optical anisotropy. They become strongly anisotropic when brushed with dry cloth, absorbent cotton, or laboratory tissue paper. The absorption becomes polarized along the direction of the brushing, indicating

that the molecules are aligned with their long axis parallel to the brushing direction. By the mechanical brushing many scratches are introduced. When viewed between crossed polarizers the scratches are light, while unscratched region remains dark, indicating that only molecules along the scratches are oriented in the brushing direction (Fig. 1). By repeating the brushing several times numerous scratches

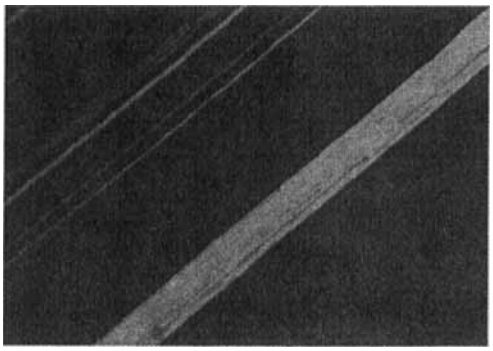


FIGURE 1 A lightly brushed film of Congo Red observed with crossed polarizers. Scratched region appears light due to double refraction, while unbrushed part remains isotropic and hence dark.

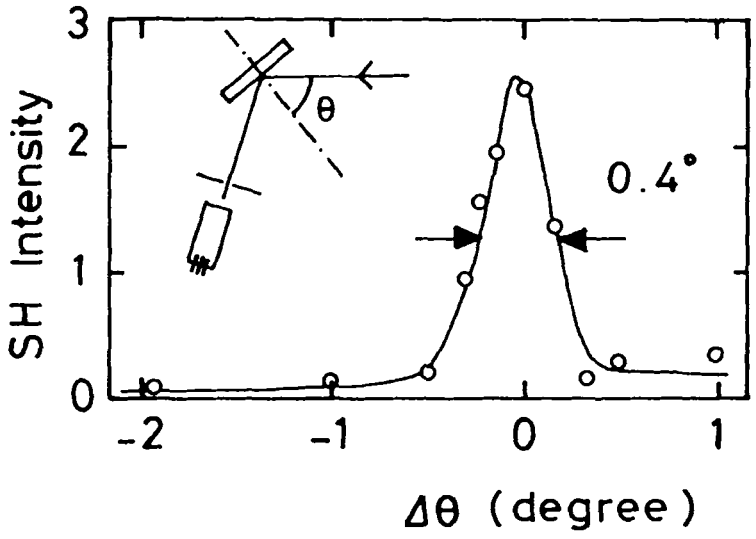


FIGURE 2 *The SH (532 nm) generated at the Congo Red thin film has a small divergence. The points have been recorded by rotating the sample, with the laser and the detector fixed.*

are produced and eventually the whole field becomes light.

The surface SHG was studied by gently focusing a Nd:YAG laser pulse (1.06 μm, 10 ns, 10 mJ) onto the surface of a film and observing the second-harmonic (SH) component in the specularly reflected light. The SH is sharply collimated within ±0.5° (Fig. 2) and is clearly visible after appropriate filtering to remove the fundamental in the infrared. At the power level of the experiment (∿50 MW/cm^2) no damage of the film was observed.

The SH from a brushed film is strongly anisotropic when the sample is rotated around the normal of the surface. When the incident light is p-polarized the SH is p-polarized. The intensity is at a maximum when the incident plane is parallel to the brushing direction (i.e., ϕ=0° and 180°). No or very weak s-component can be detected. It may be noted that the brushing was made in one direction only. With s-polarized incident light a maximum is observed at ϕ=90° and at 270°, both for s-polarized and p-polarized SH. Obviously an electric field parallel to the brushing direction is effective in generating the SH.

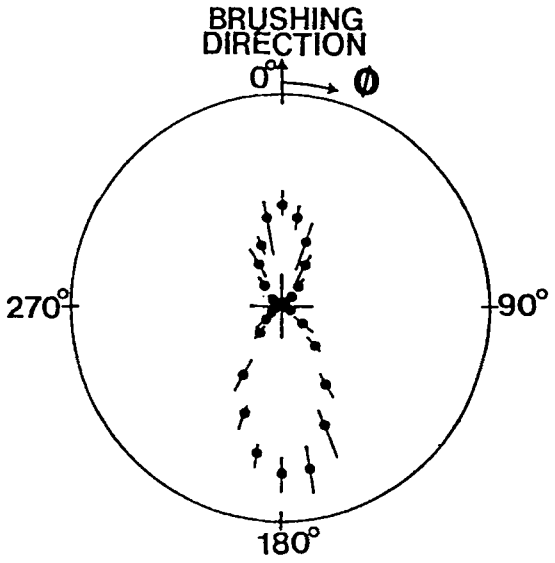


FIGURE 3 Dependence of the SH intensity on the azimuthal angle ϕ. Each experimental point is the average for five shots. Note the difference in the intensities at ϕ=0° and at 180°. The direction of the brushing is indicated by an arrow.

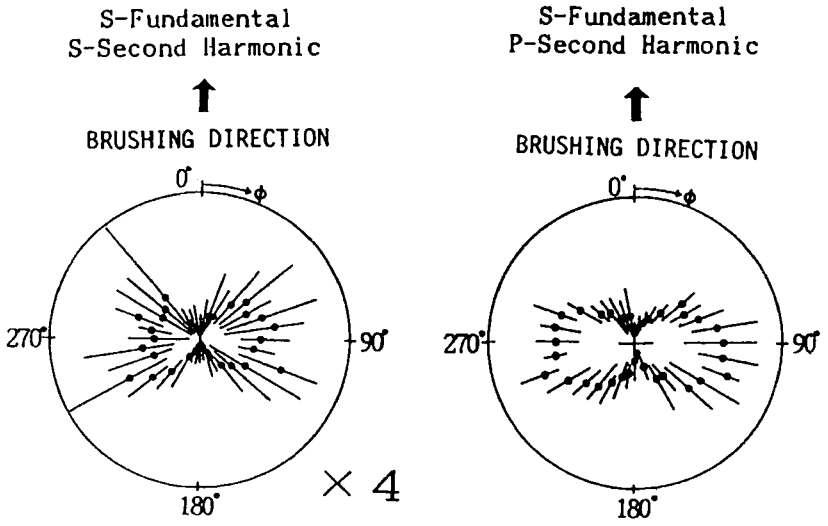


FIGURE 4 SH intensity with s-polarized incident light. Both s-polarized and p-polarized SH are generated, the latter being more intense. The scale for s-polarized SH is multiplied by 4.

The SH from the brushed film is several times more intense than that from as-coated (unbrushed) films. Further enhancement of the SHG is possible by utilizing the total reflection near the critical angle. As is well known in ATR spectroscopy, the interaction length of light with the surface becomes effectively longer with total reflection. An enhacement of more than one order of magnitude has been realized.

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