

approximations used in the theoretical treatment of below-bandgap optical nonlinearities in confined systems.

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#### Characterization of nonlinear macromolecules at surfaces

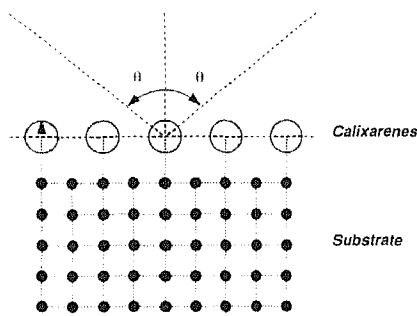
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The nonlinear optical properties of the macromolecule nitrocalix[4]arene have been studied by means of surface second-harmonic generation (SSHG). Those properties are controlled by the polarizability and hyperpolarizability tensors  $\alpha(\omega)$ ,  $\beta(2\omega)$ , ( $\omega$ : angular frequency), commonly studied in a solvent using Rayleigh and hyper Rayleigh scattering (HRS). Measurements of that type yield only limited information about the induction, given by:

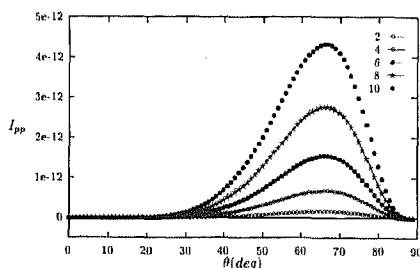
$$p(2\omega) = \vec{\alpha}(2\omega)E_L(2\omega) + \vec{\beta}(2\omega)E_L(\omega)E_L(\omega) \quad (1)$$

due to orientational averaging ( $p$ : dipole strength,  $E_L$ : local field). More complete characterization can be obtained by aligning the molecule in space. For solvents this requires strong electric fields, but surfaces build an alternative way to align the macromolecules. The drawback of a significant reduction of the measured volume becomes compensated by the specular nature of SSHG. This usage of SSHG we want to support in our contribution by making suitable model calculations. *In situ* characterization requires the environment (i.e., the substrate) to be properly accounted for. Classically this is done by means of Fresnel equations, which describe the substrate as a continuum. Simultaneous discrete description of the calixarenes is problematic, but that problem can be overcome by using a discrete description for the substrate as well. This we have done by extending our discrete, linear technique to solve the reflection problem<sup>1-3</sup> to nonlinear cases.

We have modelled the substrate by a simple cubic lattice with lattice parameter  $0.5a$ , and Clausius-Mossotti derived linear polarizabilities, corresponding to a refractive index of 1.47 (Fig. 1). The calixarenes are positioned on a square lattice (lattice parameter  $a = 10 \text{ \AA}$ ), where the calix-sites are on top of one of the substrate sites. Substrate-calix spacing is

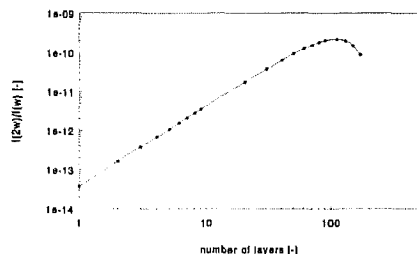


QThF4 Fig. 1. Calixarenes on glass substrate (model).



QThF4 Fig. 2.  $p$ -type  $2^{\text{nd}}$  harmonic intensity for several layer thicknesses of calixarenes and function of angle of incidence  $\theta$ .

#### SH on calix[4]arenes pp analyses



QThF4 Fig. 3. Maximum pp-intensity for varying  $\theta$ , as a function of number of layers of calixarenes.

$0.75a$  and the mutual spacing of the calix layers is  $2a$ . The nonlinear behaviour of the calix-molecules is taken uniaxial<sup>4</sup> with  $\beta_{zzz} = 1.11 \times 10^{-49} \text{ Fm}^3/\text{V}$  and the isotropic linear behaviour corresponds with refractive indices  $n(\omega) = 1.565$  and  $n(2\omega) = 1.535$ , where  $\hbar\omega = 1.165 \text{ eV}$ . We have changed two parameters essential for characterization. First we have varied the angle of incidence  $\theta$  for varying number of layers of calixarenes. Results are shown in Fig. 2, with the nonlinear axis perpendicular to the surface. The maximum obtained in reflection varies from  $67^\circ$  initially to  $71^\circ$  for 170 layers. This maximum is given for varying layer thickness in Fig. 3, where up to 150 layers quadratic behaviour is displayed. This corresponds with a constant local field effect and represents the volumetric regime. Since in this regime the total intensity depends only on the measured volume, SHG can be used to determine

thickness if the area is known. Above 150 layers the curve declines as a result of interference.

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#### Dual frequency interferences in organic materials

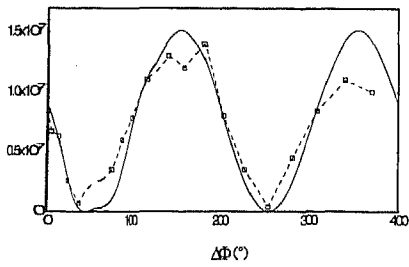
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Second-harmonic generation has been observed in glass optical fibers<sup>1</sup> prepared by an intense light at 1064 nm with a simultaneous seeding light at double frequency, although the centrosymmetric structure of silica forbids any second-order optical nonlinearity. It can be interpreted in terms of nonclassical holographic processes with coherent multifrequency fields.<sup>2</sup> Indeed the interference between a light wave and its second harmonic leads to a nonzero average cube of the optical field resulting of the coherent superposition of the two fields at  $\omega$  and  $2\omega$  frequencies. In glass, however, the magnitudes of the induced nonlinearities remain quite weak. In view of these limitations a new breakthrough has emerged after recent demonstration of photoinduced bulk transient  $\chi^{(2)}$ -grating in organic solutions. Indeed large benefit can be derived from highly nonlinear molecules and the potentiality of molecular engineering in organics is enormous.

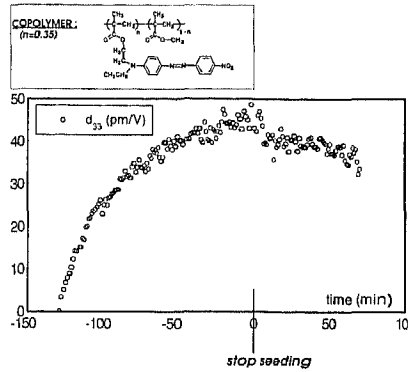
Using a pump-probe experiment in a phase-conjugation configuration, dynamical studies have lead to precise microscopic characterization and finally to a good understanding of the effective mechanism involved in organic dyes.<sup>3</sup> The process is interpreted as an orientational hole burning in the isotropic distribution of molecules. Indeed, when excited at resonance, the molecules lacking an inversion center, experience a simultaneous one- and two-photon absorption on the same  $|0\rangle \rightarrow |1\rangle$  electronic transition. This interference between one- and two-photon absorption results in a selective polar excitation of the molecules and thus in a macroscopic susceptibility  $\chi^{(2)}$  distributed in a grating with a period satisfying the conditions of phase matching between pump and second-harmonic waves:

$$\chi^{(2)} \propto \langle (E(\mathbf{M}, t) = E_\omega(\mathbf{M}, t) + E_{2\omega}(\mathbf{M}, t))^3 \rangle_t = E_{2\omega}(\mathbf{M})E_\omega(\mathbf{M})E_\omega(\mathbf{M}).$$

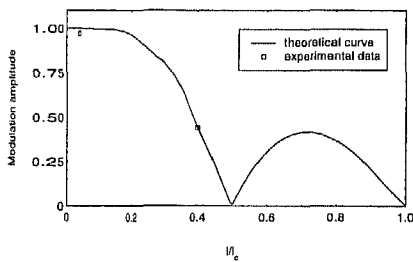
We report here on the quasi-permanent recording of photoinduced  $\chi^{(2)}$ -grating in spin-coated azo dye doped polymers.<sup>4</sup> In-



**QTh5 Fig. 1.** Experimental dependence of the second-harmonic signal intensity (in arbitrary units) with the relative phase  $\Delta\Phi$  of the  $\omega$  and  $2\omega$  writing beams. This signal intensity was recorded after a 20-minute preparation of the sample ( $\omega$  and  $2\omega$  writing beams simultaneously incident on the sample). The sample was a 0.1- $\mu\text{m}$  spin-coated film of copolymer of Disperse Red 1 (DR1) in polymethylmethacrylate (PMMA). The source was a passively and actively mode-locked  $\text{Nd}^{3+}$ -YAG laser delivering 25 psec pulses at 1064 nm at a repetition rate of 10Hz, the weaker second-harmonic beam being obtained after frequency doubling in a KDP crystal. The continuous curve corresponds to theoretical dependence.



**QTh5 Fig. 3.** Experimental growth and decay of the second-harmonic susceptibility  $d$  ( $d = \chi^{(2)}/2$ ) derived from the second-harmonic signal intensity for a 0.5- $\mu\text{m}$  spin-coated film of side-chain copolymer of DR1 in PMMA (after optimization of the energy balance between the  $\omega$  and  $2\omega$  writing beams). The intensities of the  $\omega$  and  $2\omega$  writing beams were respectively 3  $\text{GW}/\text{cm}^2$  and 30  $\text{MW}/\text{cm}^2$  and were thus in good agreement with the optimized theoretical balance corresponding to equal one- and two-photon absorption probabilities.



**QTh5 Fig. 2.** Theoretical dependence of the amplitude of modulation of the second-harmonic signal intensity with the thickness of the sample  $l_c$ . The experimental points were obtained from spin-coated films of side-chain copolymer of DR1 in PMMA (synthesized by polymerization of a 35/65 molar mixture of DR1-MMA in MMA).

deed in polymer matrices, orientational motions are frozen and the dual frequency interference process results in an effective poling of the medium via Trans-Cis isomerization processes.<sup>5</sup> The interference pattern can then be characterized by reading of this hologram by second-harmonic generation:

$$E_{2\omega}^{SHG} = \chi^{(2)} E_{\omega}^2.$$

By varying the relative phase  $\Delta\Phi$  of the  $\omega$  and  $2\omega$  writing beams, we observe indeed a sinusoidally-modulated signal intensity with period  $2\Delta\Phi$  (Fig. 1). Modulation amplitude strongly depends on the ratio of the thickness  $l$  of the sample to the coherence length  $l_c$  (Fig. 2), as expected theoretically. Importantly the transition probability between ground and the first excited state is the sum of three terms: a one-photon transition term, a two-photon transition term, and an inter-

ference term between one- and two-photon transitions. The last term is the only one responsible for the polar excitation of the dye molecules. A compromise must be found between the relative energy of the  $\omega$  and  $2\omega$  writing fields in order to optimize the weight of the polar term with respect to the nonpolar terms and thus to maximize the contrast of the orientation-selective excitation. Efficiency of the process is strongly dependent on the balance between  $\omega$  and  $2\omega$  intensities. Comparing the induced second-harmonic signals, we clearly show that it is possible to reach  $\chi^{(2)}$ -values as large as that obtained from polarization techniques (such as Corona poling) of the same material (Fig. 3).

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