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Influence on SSHG of the orientation of uniaxial molecules on surfaces

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Abstract

The nonlinear optical behaviour of an unidirectionally oriented monolayer of macromolecules at a substrate is studied by means of the discrete dipole model. Polar and azimuthal dependence of the second harmonic pp-reflectance has been investigated. For tilted molecules two minima are found.

Keywords: Computer simulations; Second harmonic generation; Semi-empirical models and model calculations

Surface second harmonic generation (SSHG) is a useful (optical) tool to study the behaviour of large macromolecules at solid surfaces and is used for the development of e.g. liquid crystal displays or nonlinear optical devices. Present models to interpret SSHG cannot use directly the (hyper)polarizability of the macromolecule. We show in this article that this is possible by means of an alternative description, the discrete dipole model. An additional advantage of this method is that it takes into account all linear and nonlinear local field effects, including retardation effects. We show the first results of a number of model calculations for a monolayer of nonlinear uniaxial macromolecules on a cubic lattice substrate. The actual numerical values used in the calculations, concern nitrocalix [4] arenes on glass/silicon to support ongoing experimental research in that field. However, the trend shown by these calculations, should hold in general for oriented monolayers.

The substrate is modelled as a cubic discrete dipole lattice with a lattice parameter of $0.5a$ and terminated by a (001) surface. The positive z -direction is along the surface normal and points towards the crystal interior. The incoming electromagnetic plane wave has electric field $E(\mathbf{r}, t)$:

$$E(\mathbf{r}, t) = E_0 \hat{\mathbf{e}} \exp(i[\mathbf{k}\mathbf{r} - \omega t]), \quad (1)$$

with amplitude E_0 and polarisation direction $\hat{\mathbf{e}}$. The wave vector is \mathbf{k} and frequency ω . The angle between \mathbf{k}_{\parallel} and one of the surface crystallographic directions is the anisotropic azimuth Ω . The angle of incidence θ_i has its usual meaning. Systems of this kind obey parallel translational symmetry and the characteristic dipole \mathbf{p}_i for plane i gets induced by the local field E_i^L , as [1]:

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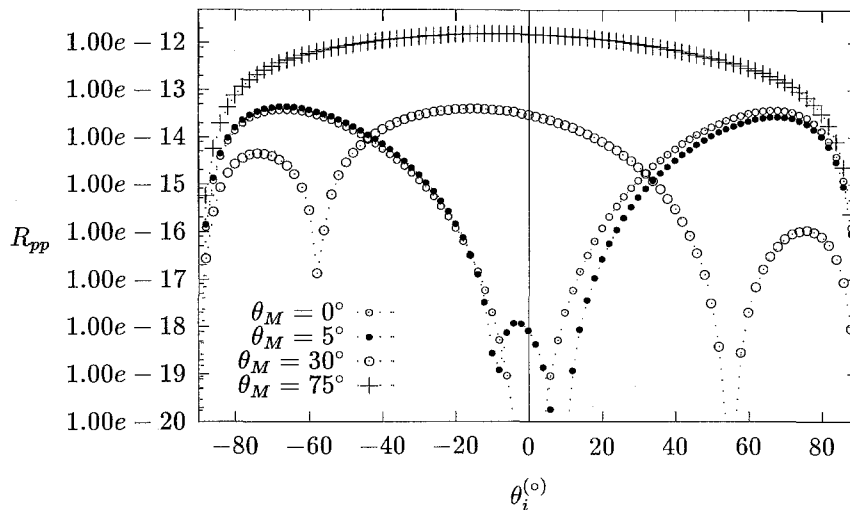


Fig. 1. pp-type second harmonic reflectance as a function of θ_i for Calix on glass ($\Omega = 0^\circ$, $\theta_M = 0.0^\circ, 5.0^\circ, 30.0^\circ, 75.0^\circ$, $r_{\text{Ani}} = 1.0$).

$$\begin{aligned}
 \vec{p}_i(1) &= \vec{\alpha}_i(1) \vec{E}_i^L(1), \\
 \vec{p}_i(2) &= \vec{\alpha}_i(2) \vec{E}_i^L(2) + \vec{\beta}_i(2) \vec{E}_i^L(1) \vec{E}_i^L(1)
 \end{aligned}
 \tag{2}$$

where $\vec{\alpha}_i$ is the polarisability tensor and $\vec{\beta}_i$ the hyper-polarisability tensor, for which we will use the symmetry arguments of the corresponding nonlinear susceptibilities. The numbers 1 and 2 are shorthand for the fundamental and second harmonic frequency, respectively. The tensor $\vec{\alpha}_i$ will always be given in units of $\alpha_0 = 4\pi\epsilon_0 a^3$. The local field \vec{E}_i^L is obtained by means of planewise summation and techniques to calculate this field efficiently, can be found in Refs. [2,3]. The bulk dipole strengths can be written as normal modes:

$$\vec{p}_{\nu V} = \sum_{m=1}^M v_m \mathbf{u}_{m\nu} e^{iq_m \nu d_B},
 \tag{3}$$

where $\vec{p}_{\nu V}$ is the dipole strength belonging to site ν of the V 'th bulk unit cell, having height d_B . Only the normal mode strength v_m , can be affected by phenomena taking place in the surface region. A crystalline semi-infinite discrete dipole system can be solved exactly by means of the double cell method [3]. This requires a subdivision of the system into a (thin) surface region and a (semi-infinite) bulk region, described by normal modes. The linear double cell method can easily be extended to the nonlinear case for the linear substrates assumed in this paper. We ignore effects of beam depletion and higher than second harmonics. The double cell interaction equations are for the fundamental frequency (\hat{i} is generic for the direction of the analyser s/p):

$$\begin{vmatrix} \mathcal{M}_{\text{SS}}(1) & \mathcal{M}_{\text{SB}}(1) \\ \mathcal{M}_{\text{BS}}(1) & \mathcal{M}_{\text{BB}}(1) \end{vmatrix} \begin{vmatrix} \vec{p}_j(1) \\ v_m(1) \end{vmatrix} = \begin{vmatrix} \vec{E}_j \\ (\hat{i} \cdot \hat{e}) E_0 \end{vmatrix}
 \tag{4}$$

and for the second harmonic frequency:

$$\begin{vmatrix} \mathcal{M}_{\text{SS}}(2) & \mathcal{M}_{\text{SB}}(2) \\ \mathcal{M}_{\text{BS}}(2) & \mathcal{M}_{\text{BB}}(2) \end{vmatrix} \begin{vmatrix} \vec{p}_j(2) \\ v_m(2) \end{vmatrix} = \begin{vmatrix} \vec{\alpha}_j^{-1}(2) \vec{\beta}_j(2) \vec{E}_j^L(1) \vec{E}_j^L(1) \\ 0 \end{vmatrix}.
 \tag{5}$$

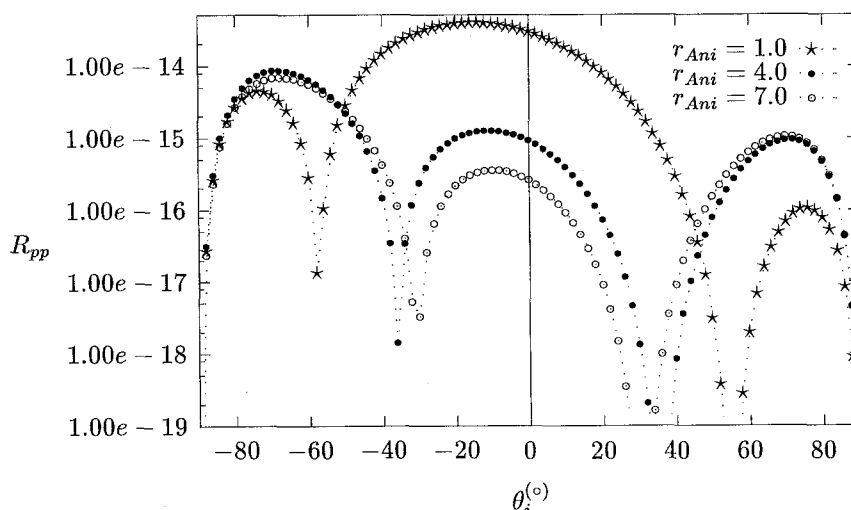


Fig. 2. pp-type second harmonic reflectance as a function of θ_i for Calix on glass ($\Omega = 0^\circ$, $\theta_M = 30.0^\circ$, $r_{Ani} = 1.0, 4.0, 7.0$).

The subscripts S and B refer to surface or bulk, respectively. The detailed expressions for the matrix elements of the sub-matrices shown in (4) are given in Ref. [3]. Subsequent solution of these two sets of equations yields the nonlinear sources ($p_i(2), v_m(2)$). From the sources for the second harmonic frequency, the nonlinear reflection coefficient $r_t(2)$ can be obtained by means of:

$$r_t(2) = \frac{2\pi i a^3 k^2}{S |k_z|} \left[\frac{\hat{i} \cdot \left(\sum_{j=1}^{\infty} e^{-ikr_j} p_j(2) \right)}{\alpha_0 E_0} \right], \quad (6)$$

where the dipole strengths for the bulk region have to be obtained from Eq. (3) and S is the area of the surface unit cell. Eq. (6) connects directly microscopic and macroscopic response.

In this article we will concentrate on monolayers and consider only pp-type second harmonic reflectances, since those have the more pronounced behaviour. To investigate the influence of the orientation of the molecule, we can rotate (hyper)polarizabilities, by means of [4]:

$$\alpha_{pq}^L(\theta_M) = \sum_{i,j} S_{pi} \alpha_{ij}^M (S^{-1})_{jq}, \quad (7)$$

$$\beta_{pqr}^L(\theta_M) = \sum_{i,j,k} S_{pi} \beta_{ijk}^M (S^{-1})_{jq} (S^{-1})_{kr}. \quad (8)$$

All adsorbed macromolecules rotate in the xz -plane over the same angle θ_M with respect to the surface normal. S is the rotation matrix and superscripts L and M refer to laboratory and molecule frame of axes.

The macromolecules are positioned on a square lattice (lattice parameter $a = 10 \text{ \AA}$), where the molecule sites are on top of one of the substrate sites of the cubic bulk lattice [5]. The fundamental frequency has been given the value $\hbar\omega = 1.165 \text{ eV}$ of a Nd:YAG laser and $E_0 = 10^7 \text{ V/m}$. The linear polarizabilities of the substrate have been Clausius–Mossotti derived from a refractive index of 1.47, in the case of borosilicate glass. For silicon substrates we have used a dielectric constant of 12.466 for the fundamental and $17.2241 + i0.4296$ for the second harmonic frequency. Substrate molecule spacing is $0.75a$. The nonlinear behaviour of the macromolecules is taken uniaxial [6], with $\beta_{zzz} = 1.11 \times 10^{-49} \text{ Fm}^3/\text{V}$ and the isotropic linear behaviour corresponds with refractive indices $n(1) = 1.565$ and $n(2) = 1.535$.

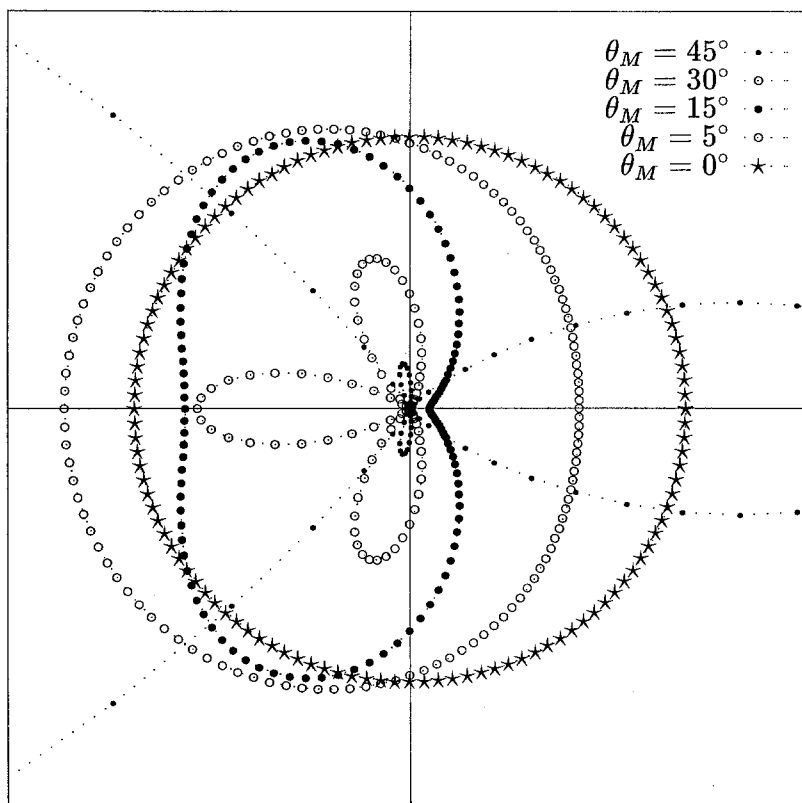


Fig. 3. pp-type second harmonic reflectance as a function of Ω for Calix on glass ($\theta_i = 45.0^\circ$, $\theta_M = 0.0^\circ, 5.0^\circ, 15.0^\circ, 30.0^\circ, 45.0^\circ$, $r_{\text{Ani}} = 1.0$. Scale: $R_{\text{pp}}(\star) = 1.0261 \times 10^{-14}$).

We start with calculation of the second harmonic pp-reflectance as a function of θ_i (polar plot), assuming an isotropic polarizability for the macromolecule. Results are shown in Fig. 1, where we have investigated several tilt angles θ_M of the molecule. For zero tilt angle and perpendicular incidence the reflectance becomes zero and at $\theta_i \approx \pm 70^\circ$ are maxima. Increasing the tilt angle until about $+45^\circ$ causes the appearance of two minima at roughly symmetrically located angles of incidence. The minimum at positive angles of incidence can be understood directly from Eq. (5). For local fields being at right angles with the molecular axis, the inhomogeneous term disappears, causing a minimum. The interpretation of the other minimum follows later. For still higher tilt angles an uninterrupted profile shows up, as the one shown for $\theta_M = +75^\circ$. Except for the special tilt angles $\theta_M = 0^\circ, +90^\circ$ all curves are asymmetric in θ_i . The overall strength of the nonlinear reflectance depends strongly on θ_M .

Also the position of the minima clearly depends on θ_M . A continuum model, where the molecule resides below the surface and gets excited by the refracted field, yields within a few degree minima at the same θ_i . However it is not consistent to assume simultaneously isotropic linear behaviour and uniaxial nonlinear behaviour for the macromolecule. Keeping the trace of the polarizability tensor constant, we have made the polarizability anisotropic through:

$$\alpha_{zz}^M = r_{\text{Ani}} \alpha_{xx}^M = r_{\text{Ani}} \alpha_{yy}^M, \quad (9)$$

where r_{Ani} is the anisotropy ratio. For several values of this ratio Fig. 2 shows the polar plot. The anisotropic

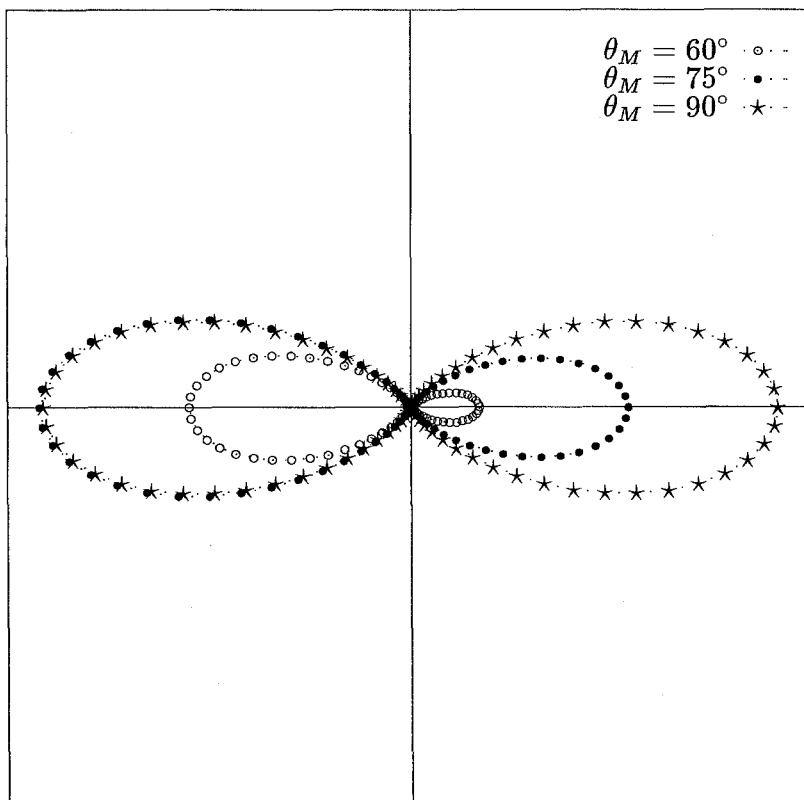


Fig. 4. pp-type second harmonic reflectance as a function of Ω for Calix on glass ($\theta_i = 45.0^\circ$, $\theta_M = 60.0^\circ, 75.0^\circ, 90.0^\circ$, $r_{\text{Ani}} = 1.0$. Scale: $R_{\text{pp}}(\star, \Omega = 0^\circ) = 1.0013 \times 10^{-12}$).

results have similar behaviour as the isotropic ones, but the position of the minima is a function of the anisotropy. This dependence clearly goes beyond a simple Fresnel-like description, since the anisotropy involves only the monolayer. It turns out that the position of the minima depends on at least two independent parameters. Consequently those minima alone cannot be used to isolate θ_M .

We have also investigated silicon substrates, to study the influence of substrate optical absorption. A silicon substrate causes no big qualitative changes. Apart from shifts of the minima due to the different substrate refractive index, the minima at negative θ_i become broader and less deep. This contains an important clue as to their origin. The direction of the induced second harmonic dipole strength is near the molecular axis and this direction in turn can be at right angles to \hat{i} . This is the Brewster configuration, which causes minima, as treated by us for the linear case. How the optical absorption of the bulk influences the minimum, can be understood along the lines of thought given in Ref. [3]. Further the absorbing substrate adds to the asymmetry of the curves.

Most experimental work in this field reports the second harmonic reflectance as a function of Ω (azimuthal plots). We have calculated those and show the results in Figs. 3 and 4 for $\theta_i = 45.0^\circ$. The lower tilt angle results ($\theta_M \leq +45.0^\circ$) are in Fig. 3. For $\theta_M = 0^\circ$ an isotropic reflectance pattern is found, as expected. Increasing θ_M to 5.0° causes the curve to shift to the left and getting oblate at one side. Along the x -direction two kinks develop for $\theta_M = +15.0^\circ$ and higher. Through 2, 3 and 4-lobe inbetween stages the higher tilt angle behaviour appears, shown in Fig. 4. Simultaneously the reflectance increases strongly and a symmetric x -oriented two-lobe

pattern for $\theta_M = +90^\circ$ is obtained. The stronger emission always takes place in a direction away from the tilt of the macromolecule.

Azimuthal plots for optically anisotropic macromolecules are qualitatively not different from isotropic ones. Hence the shape of the pp-plots does not learn about the amount of anisotropy. Azimuthal plots at the minimum positions could be an exception. Those we have calculated for $r_{\text{Ani}} = 1.0$ and 4.0 . At the corresponding minima exactly the same patterns were obtained, only differing in strength. Independent information about the anisotropy has to be obtained in another way, e.g. from linear anisotropy measurements (ellipsometry). Only after that, calculations of this type can be used to determine θ_M by means of SSHG.

Results reported in the literature are among others by Hollering [7], who studied polar plots for the hemicyanine/glass system and by Feller [8], who studied azimuthal plots for 8CB on several types of substrate. Most plots they have measured come close to one of the plots we have investigated, but since none of their samples is sufficiently unidirectional a direct comparison cannot be made. The majority of the studies in this field (e.g. Rasing et al. [9]), convert uniaxial molecular hyperpolarizabilities to second harmonic susceptibilities, having two components governed by the tilt angle. These two components are used to isolate the tilt angle, but such approach will not work for this discrete model, where no susceptibilities are used. The pp-minima which have been calculated in this paper, have not been found yet experimentally, as far as we know. Either theoretically a suitable averaging procedure has to be added to these calculations or experimentally better controlled samples have to become available. We hope to report about such work in the near future.

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