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Second-harmonic generation in quinquethienyl monolayers

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Well-organized monolayers of quinquethienyl (QT) have been studied by second-harmonic generation (SHG). Due to the properties of the molecular hyperpolarizability tensor $\alpha^{(2)}$ of QT, SHG signals originating from the direction of the surface normal, which corresponds also to the alignment direction of these molecules of rodlike structure, are symmetry-forbidden. The observed intense SHG signals under *p*-polarized excitation can either be explained in terms of anisotropic averaging, which accounts for orientational irregularities on a microscopic scale due to steric hindrance or, alternatively, by the influence of an external, symmetry-breaking, static electric field acting on the individual molecules and arising from their noncentrosymmetric environment.

I. INTRODUCTION

The conversion of light of fundamental frequency ω into radiation of frequency 2ω—second-harmonic generation (SHG)—is governed by the condition of noncentrosymmetry.[1] Therefore studies incorporating surface effects have gained in scientific interest for SHG, since surface layers are intrinsically noncentrosymmetric.[2–4] A number of recent papers[5–7] discuss SHG in well-orientated monolayers of Langmuir-Blodgett type.[8] Due to their high surface sensitivity, SHG techniques have developed into a very useful tool for probing molecular orientation, provided the molecules of the layer under investigation show the required anisotropy. In this investigation we consider monomolecular layers of molecules of exact or near-C_{2v} symmetry. These molecules possess a long axis which in the layer is inclined by a small angle with respect to the surface normal. If the twofold symmetry axis of an individual molecule is parallel to the long axis, as has been the case in previous investigations,[2–4] isotropic averaging over molecular orientations around the surface normal leads to resulting nonvanishing signals. On the other hand, if the twofold axis is perpendicular to the long axis, the same averaging procedure leads to zero intensity for SHG. As in the latter case we have detected nonvanishing signals three orders of magnitude above background, we must conclude that either the monolayer exhibits anisotropies on a molecular scale which account for the observed SHG signals, or the asymmetry of the environment breaks the symmetry of the molecular hyperpolarizability tensor, leading to a nonvanishing value for $\alpha^{(2)}_{z'z'z'}$. After a brief description of the experimental setup and results, these different approaches for an explanation will be discussed in terms of (a) an orientational model, and (b) a polarization model.

II. EXPERIMENTAL RESULTS

Assuming isolated, noninteracting molecules, the macroscopic nonlinear susceptibility $\chi^{(2)}_{xyz}$ is related to the microscopic nonlinear polarizability $\alpha^{(2)}_{x'y'z'}$ by the relation

$$\chi^{(2)}_{xyz} = N_s \cdot L_{xyz} \cdot \langle T^{x'y'z'}_{xyz} \rangle \cdot \alpha^{(2)}_{x'y'z'} \ . \tag{1}$$

Equation (1) describes the transformation from the molecular coordinate system (x',y',z') to the laboratory frame (x,y,z) by means of the transformation matrix $T^{x'y'z'}_{xyz}$, the molecular surface coverage density N_s, and the local-field correction L_{xyz}. Any orientational assumption enters into the averaging process denoted by the symbol $\langle T^{x'y'z'}_{xyz} \rangle$.

We neglect the local-field corrections in our calculations because we are primarily interested in relative polarization effects and only secondarily in the absolute magnitude of the measured nonlinear-optical quantities. The problem of local-field corrections in Langmuir-Blodgett (LB) sample geometries has been discussed in detail in Ref. 9.

So far, orientational analyses have been performed under the assumption that one particular component of the $\alpha^{(2)}$ tensor dominates. In this case, measurements using various combinations of polarizations have permitted a determination of an average molecular orientation. The result of such an orientation measurement must evidently be independent of the wavelength used in the experiment. This has been demonstrated quite convincingly by Heinz *et al.*[10] for the case of the orientation of γ-nitrobenzoic acid (*p*-NBA), where the component $\alpha^{(2)}_{z'z'z'}$ dominates. Hence the orientation of a *p*-NBA monolayer can be conveniently described by the average orientational angle of the molecular axis with respect to the surface normal.

In the present investigation we have studied monolayers of quinquethienyl[11,12] (QT) as shown in Fig. 1. In this molecule the C_2 symmetry axis is perpendicular to the molecular long axis. The average coverage density ratio between the layer-stabilizing agent C_{20} and QT was 3:1 and the layers, originally prepared on a water surface, were subsequently transferred to quartz glass slides for SHG measurements in Fresnel geometry or in total internal reflection geometry in order to raise the signal lev-

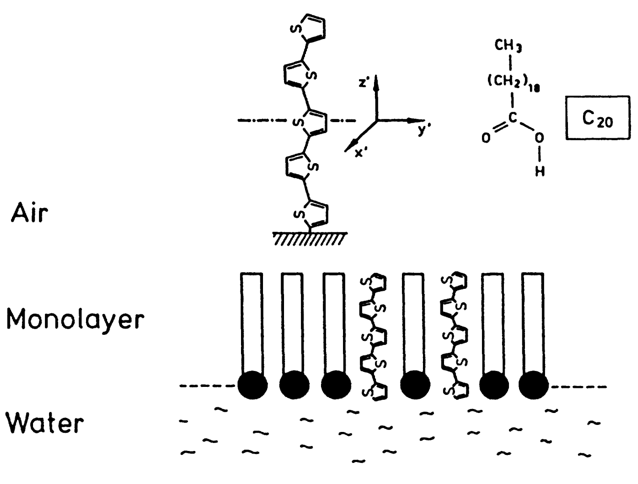


FIG. 1. Schematic view of QT monolayers prior to preparation on quartz substrates, together with molecular coordinate system.

el.[13,14] According to Refs. 11 and 12 the QT orientation was carefully checked with linear-optical techniques and the QT molecules found to be nearly completely oriented between the C_{20} stabilizer as indicated in Fig. 1. Figure 2 shows the surprising result in terms of four spectra displaying the linear and nonlinear response under s- and p-polarized excitation with $\bar{E}(\omega)$ in the wavelength range 300–550 nm. For the SHG measurement the fundamental wavelength was carried between 680 and 1064 nm. Both the linear and nonlinear spectra are dominated by the strong QT response under p-polarized excitation in this wavelength range, suggesting that both polarizations $\bar{P}(\omega)$ and $\bar{P}(2\omega)$ oscillate parallel to the surface normal.

III. DISCUSSION

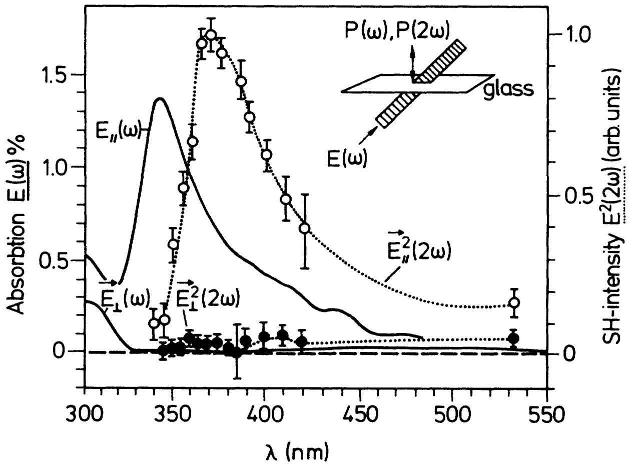


FIG. 2. Linear $[E(\omega)]$ and nonlinear $[E(2\omega)]$ response of QT monolayers between 300 and 550 nm.

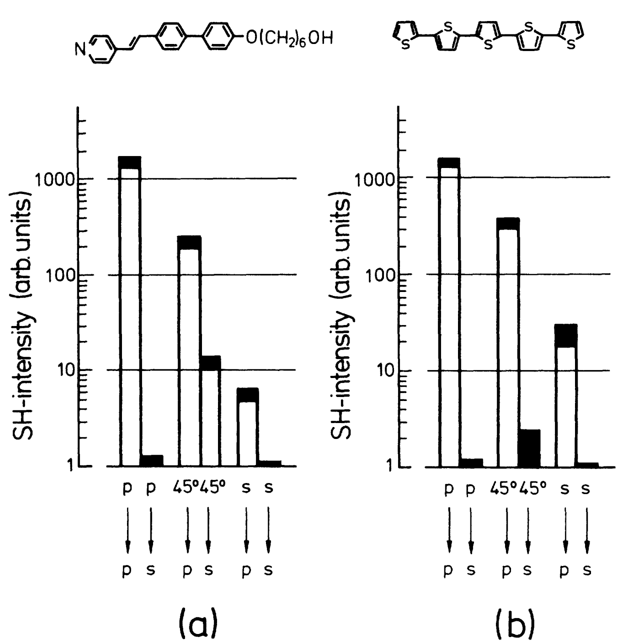


FIG. 3. Histograms of SHG signals excited by various polarization directions of the incident fundamental radiation and analyzed for s- and p-polarized components: (a) a typical pyridine derivative taken from Ref. 15 with $\alpha^{(2)}_{z'z'z'}$ dominant, (b) QT upon excitation at 730 nm.

We now discuss this experimental result in terms of the molecular tensor elements for $\alpha^{(2)}$. Figure 3(a) shows in a convenient histogram the polarization-dependent SHG response of an azastilbene derivative, studied in some detail in Ref. 15 as an example for a case in which the $\alpha^{(2)}_{z'z'z'}$ tensor element predominates. Although the histogram for QT looks quite similar [Fig. 3(b)], the same interpretation cannot be applied to a well-organized layer of this substance. Since the twofold C_2 axis of QT (cf. Fig. 1) is parallel to the molecular y' axis, the condition holds

$$\alpha^{(2)}_{z'z'z'} \equiv 0 \; . \tag{2}$$

Symmetry requirements allow only the following molecular tensor elements to be nonvanishing in QT (see Table I):

$$\alpha^{(2)}_{x'x'y'},\quad \alpha^{(2)}_{z'z'y'},\quad \alpha^{(2)}_{y'y'y'},\quad \alpha^{(2)}_{y'x'x'},\quad \alpha^{(2)}_{y'z'z'} \; .$$

Additional, semiempirical quantum-chemical calculations[16] indicate that

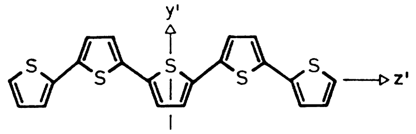
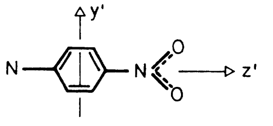
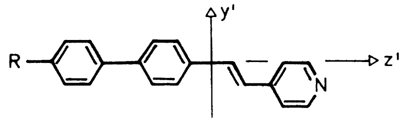
$$\alpha^{(2)}_{z'z'y'} \approx \alpha^{(2)}_{y'z'z'} > \alpha^{(2)}_{y'y'y'} > \alpha^{(2)}_{x'x'y'} \approx \alpha^{(2)}_{y'x'x'} \tag{3}$$

in the long-wavelength range far removed from the first electronic absorption of QT. These relations reflect the fact that the largest transition moments occur along the molecular long axis z', whereas transitions polarized in the x' direction, perpendicular to the molecular plane, play a negligible role. The definite observations of p- and s-polarized SHG signals from QT according to Figs. 2 and 3(b) must indeed be due to the components

$$\chi^{(2)}_{zxx} = \chi^{(2)}_{zyy},\quad \chi^{(2)}_{zzz},\quad \chi^{(2)}_{yyz} = \chi^{(2)}_{xxz} \; . \tag{4}$$

The equalities in (4) reflect the observed symmetry upon rotation about the surface normal or laboratory z axis.

TABLE I. Symmetry properties and molecular tensor elements.

Molecule	Symmetry	Nonvanishing molecular tensor elements[a] $\alpha^{(2)}$	Dominant element
	C_{2v} $C_2(y')$	$y'y'y$ $y'z'z', z'y'z' = z'z'y'$	none
	C_{2v} $C_2(z')$	$z'z'z'$ $z'y'y', y'z'y' = y'y'z'$	$z'z'z'$
	C_s	$z'z'z'$ $z'y'y', y'z'y' = y'y'z'$ $y'z'z', z'y'z' = z'z'y'$	$z'z'z'$

[a]Elements containing the coordinate x' are in all cases either very small or equal to zero because of the planar symmetry.

The nonoccurrence of s-polarized SHG signals under pure p- or s-polarized excitation also indicates the absence of any anisotropy around the surface normal.

The difference in the wavelength dependence of $E_{\parallel}(2\omega)$ and of $E_{\perp}(2\omega)$ in Fig. 2 suggests that the signals are not mainly due to a single dominant molecular tensor component. If this were the case, both the $\parallel$ and $\perp$ signal would show a resonance peak at the same wavelength. Since the obvious component $\alpha^{(2)}_{z'z'z'}$ usually responsible for the strong SHG signals under p excitation is here symmetry-forbidden, we are forced to seek another interpretation for the measured data.

The macroscopic rotational (near) isotropy around the surface normal is supported by the very weak $p \rightarrow s$ and $s \rightarrow s$ signals in Fig. 3(b). For $\lambda \leq 300$ nm, where y'-polarized transitions in QT come into play, these signals rise slightly above the noise level but remain small.[17]

In the following we try to interpret these experimental results (a) in terms of an appropriate orientational averaging, assuming $\alpha^{(2)}_{z'z'z'} = 0$; or as an alternative (b) in terms of a symmetry-breaking external electric field acting on the molecules on the surface and leading to $\alpha^{(2)}_{z'z'z'} \neq 0$.

A. Orientational model

Here we consider an anisotropic microscopic molecular distribution which is comparable with the observed macroscopic (near) isotropy. As usual we relate the molecular coordinate system to the laboratory frame by the Euler angles θ (inclination with respect to the surface normal), ϕ (rotation around the surface normal), and ψ (rotation around the molecular long axis). We have

$$\langle T_{xyz}^{x'y'z'} \rangle = \langle A_{x'x} A_{y'y} A_{z'z} \rangle , \tag{5}$$

where A designates the Euler angle matrix.[18] We notice that *isotropic* averaging over the angle ϕ *only*, for arbitrary and fixed values of θ and ψ, can lead to a distribution compatible with the observed macroscopic symmetry,

$$\begin{aligned}
\chi_{15}^{(2)} &= \chi_{24}^{(2)} \\
&= \tfrac{1}{2}[B\alpha^{(2)}_{y'y'y'} - A\alpha^{(2)}_{y'z'z'} + (D - A)\alpha^{(2)}_{z'z'y'}] , \\
\chi_{31}^{(2)} &= \chi_{32}^{(2)} \\
&= \tfrac{1}{2}(B\alpha^{(2)}_{y'y'y'} + D\alpha^{(2)}_{y'z'z'} - 2A\alpha^{(2)}_{z'z'y'}) , \\
\chi_{14}^{(2)} &= -\chi_{25}^{(2)} = \tfrac{1}{2}E(\alpha^{(2)}_{y'z'z'} - \alpha^{(2)}_{z'z'y'}) , \\
\chi_{33}^{(2)} &= C\alpha^{(2)}_{y'y'y'} + A(\alpha_{y'z'z'} + 2\alpha^{(2)}_{z'z'y'}) ,
\end{aligned}$$

where

$$\begin{aligned}
A &= \langle \cos\psi \cos^2\theta \sin\theta \rangle , \\
B &= \langle \cos\psi \sin^2\psi \sin\theta + \cos^3\psi \cos^2\theta \sin\theta \rangle , \\
C &= \langle \cos^3\psi \sin^3\theta \rangle , \\
D &= \langle \cos\psi \sin^3\theta \rangle , \\
E &= \langle \sin\psi \cos\theta \sin\theta \rangle .
\end{aligned} \tag{6}$$

The quantities A to E depend on the angles θ and ψ, and the brackets then imply an *isotropic* averaging over these angles weighted by a corresponding distribution function which would have to be assumed, or determined by other means. Because of the vanishingly small influence of transitions polarized perpendicularly to the molecular plane in the wavelength range of interest, we have here neglected the molecular tensor elements $\alpha^{(2)}_{x'x'y'}$ and $\alpha^{(2)}_{y'x'x'}$.

Considering the results at long wavelengths far from resonances, we notice in particular that $\chi_{14}^{(2)} = -\chi_{25}^{(2)}$ vanishes, provided the corresponding Kleinman[19] symmetry

TABLE II. Results of CNDO calculations (Ref. 16) for the QT-[$Si_2O_6H_4$] system for various distances d, as shown in Fig. 4. The computations were based on a standard parametrization and included 253 singly and 141 doubly excited configurations.

d (Å)	$\alpha^{(2)}_{z'z'z'}$ (10^{-30} esu)
∞	0
4	1.41
2	5.17
1	10.76

is fulfilled. If this is the case, then the remaining tensor elements indeed show the required isotropy with respect to the laboratory coordinates x and y. We furthermore see that the coefficients C and D depend on $\sin\theta$ to the third power. If the angle θ is small, which the experimental data clearly imply, then C and D should obviously be small compared to A, B, and E.

B. Polarization model

A second attempt to interpret the observed SHG data is based on molecular considerations. It may be assumed that the molecule QT resting at one end on the supporting glass surface and being in contact with air at the other end, gets polarized along the molecular long axis z'. The first-order polarizability $\alpha^{(1)}_{z'z'}$ is not only significant for the electronic ground state. It is particularly important for the lower excited states. This arises through the fact that some of these excited states are connected to other energetically close-lying electronic states by very large electric dipole transition moments in the z' direction. Under the influence of an external static electric field along the molecular long axis z', these states then acquire a substantial increment of dipole moment in that direction. This, in turn, contributes to a nonvanishing value for $\alpha^{(2)}_{z'z'z'}$.

We have attempted to simulate this symmetry-breaking polarization effect in performing calculations by the CNDO method[16] on a QT molecule at different distances from a $Si_2O_6H_4$ moiety (see Table II and Fig. 4). The strongly polarizing influence of the perturbation is strikingly reflected by the rapid increase of $\alpha^{(2)}_{z'z'z'}$ with decreasing distance d. The order of magnitude for $\alpha^{(2)}_{z'z'z'}$ is in agreement with the one deduced from experiments where, in contrast to the orientation model (Sec. III A), one then assumes complete isotropic averaging around the two angles ϕ *and* ψ. The results obtained by the CNDO method are qualitatively in agreement with simpler PPP calculations[20] in which the molecular perturbation is simulated by modifying the valence-state ionization potential of the terminal carbon atom at one end of the molecule.

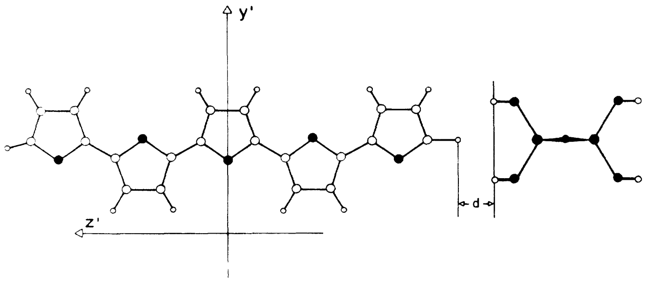


FIG. 4. Model of a QT molecule at a distance d from a $Si_2O_6H_4$ moiety.

IV. CONCLUSIONS

The study of SHG in monolayers of quinquethienyl are of particular interest because of the symmetry properties of this molecule. In contrast to a number of other compounds studied in a similar fashion, the molecular symmetry axis is not parallel but perpendicular to the molecular long axis. The observed SHG spectra can only be interpreted either in terms of a distribution of the molecules in the layer around the surface normal which is not fully isotropic, or in terms of the symmetry-breaking influence of the molecular environment on the electronic structure of the individual molecules. Although it is difficult to decide between these two possibilities, we tend to believe that molecular polarization effects may be important. In fact, additional experimental investigations revealed that both effects seem to contribute to the unexpected second-harmonic (SH) signals.

(i) Variations in composition and concentration of the SH-inactive C_{20} stabilizer changed the spectral shape of the $E_{\|}(2\omega)$ curve under p-polarized excitation (cf. Fig. 2), but did not reduce the magnitude of the SH signals. Hence different *lateral* environmental conditions influence the incomplete azimuthal averaging.

(ii) embedding the QT monolayers together with C_{20} stabilizer into a symmetric environment with respect to the *surface normal* leads to a complete disappearance of SH signals.

Further study of such symmetry-breaking influences on surfaces should be pursued. In particular, we plan to identify with greater accuracy the signals in the short-wavelength ($\lambda < 300$ nm) range.

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