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The effect of the local field on the optical second-harmonic response of mixed liquid crystal–stearic acid monolayers

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Abstract. Optical second-harmonic generation (SHG) from mixed liquid crystal–stearic acid molecular monolayers, as a function of liquid crystal concentration, is reported. It is shown that, in concentrated monolayers, a substantial local-field effect exists which can be described, to a first approximation, by a point dipole model. The apparent molecular hyperpolarizability in pure monolayers of these liquid crystals is reduced by a factor of between six and eight, due to this local field. This is an important consideration in the design of materials for ultra-thin-film non-linear optical devices. Hyperpolarizability measurements should be made using monolayer films where the active species is diluted by about a factor of ten by a species with negligible polarizability, such as a fatty acid, having first taken care to establish that the active species disperses uniformly. In this way the experimental hyperpolarizability may be directly compared to theoretical values from calculations of isolated molecular clusters. These LB monolayers are ideal model systems for testing theoretical approaches to the local-field problem, and progress in this area is important in understanding the optical response of surfaces and interfaces in general, and those of semiconductors in particular.

1. Introduction

Second-order non-linear optical techniques like second-harmonic generation (SHG) have recently been developed as extremely versatile and sensitive surface and interface probes [1–3]. SHG measurement from a molecular monolayer [4], particularly when prepared by the Langmuir–Blodgett (LB) technique (reviewed recently by Peterson [5]), is one of the best methods of determining the components of the molecular hyperpolarizability tensor, $\beta_{\xi\eta\zeta}$, which is central to evaluating the potential of the molecular species for non-linear optical applications. Values of $\beta_{\xi\eta\zeta}$ for the isolated molecular species or cluster may also be directly compared with the theoretical values from molecular structure calculations [6].

It has been known for some time that local-field effects, arising from dipolar interactions of various types, can influence SHG from thin films on surfaces [7]. LB films are particularly well suited for evaluating these effects, as the concentration, and hence nearest-neighbour distance, of the active species responsible for SHG can easily be controlled. This was recognized by Hayden [8] in an elegant study of mixed hemicyanine dye–behenic acid LB films, where a classical point dipole model [9] was used to interpret the results. For this system local-field effects become significant at a dye molecule separation of about 10 Å. This appears to be the only study of this type carried out so far, and considerable discrepancy between theory and experiment was found. Possible sources of this discrepancy included dye aggregation at higher concentrations, and dispersion of β with concentration [8].

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SHG from the cyanoterphenyl thermotropic liquid crystal, T15 (see section 3), diluted in stearic acid, has been studied in detail recently [10], and the dispersion of the SH response with excitation frequency is now well understood. This, together with the absence of aggregation problems, makes the system well suited for investigating local-field effects. SHG from the monolayer films, as a function of T15 concentration, is analysed within the framework of the point dipole model [7, 9].

2. Theory

SHG arises from the non-linear polarization $P(2\omega)$ induced by an incident laser field $E(\omega)$. The surface allowed dipole contribution can be written as

$$P_i(2\omega) = \chi_{ijk}^{(2)} E_j(\omega) E_k(\omega) \quad (1)$$

where $\chi_{ijk}^{(2)}$ is the second-order non-linear susceptibility tensor component reflecting the structure and symmetry properties of the surface layer. Large field gradients normal to the surface can also give rise to higher-order bulk non-linear polarization but, under the experimental conditions used, no SHG from the fused silica substrate was detected. The three-phase model used to describe the SH response of the monolayer has been discussed in detail previously [10], and follows the approach of Zhang *et al* [11]. It has been shown that, even at resonance, the SH response of the T15 molecule arises from a single component along the long molecular axis ζ , $\beta_{\zeta\zeta\zeta}$, and that the monolayer is optically isotropic in the plane. The molecular hyperpolarizability, $\beta_{\zeta\zeta\zeta}$, is then related to the susceptibility, χ_{ijk} , by

$$\chi_{zzz} = N_s \langle \cos^3 \psi \rangle \beta_{\zeta\zeta\zeta} \quad (2)$$

$$\chi_{zyy} = \frac{1}{2} N_s \langle \sin^2 \psi \cos \psi \rangle \beta_{\zeta\zeta\zeta} \quad (3)$$

where N_s is the surface number density of molecules and ψ is the polar (or tilt) angle of the molecule measured between the substrate surface normal, z , and the long molecular axis, ζ . The angle brackets represent an averaging over the orientational distribution, which is assumed to be narrow for good quality Langmuir–Blodgett monolayers. The average tilt angle of the molecule, $\bar{\psi}$, can be determined from

$$\tan^2 \bar{\psi} = 2\chi_{zyy}/\chi_{zzz}. \quad (4)$$

However, these relations where the macroscopic susceptibility is proportional to the number of molecules present are only valid for dilute media. Where the atoms or molecules are closely packed, the induced-dipole–induced-dipole interaction becomes important and is treated in terms of the local field it generates. The susceptibility, χ_{ijk} , is no longer simply proportional to the molecular hyperpolarizability, $\beta_{\zeta\zeta\zeta}$, the difference being described by a correction factor which takes into account the change in the local field at each molecule due to the surrounding induced dipoles.

The usual derivation of the local-field correction only applies to isotropic or cubic media with well-localized bound electrons. The effective second-order polarizabilities incorporating the local-field correction factors for SHG are written in the laboratory frame as

$$\beta_{ijk}^{\text{eff}} = L(2\omega)L(\omega)^2 \beta_{ijk} \quad (5)$$

with $L = (\epsilon + 2)/3$, where L is the local-field correction factor and ϵ is the dielectric function, at frequency ω or 2ω [12]. It can be seen that a correction factor must be present for each field component, and that isotropic local fields *increase* the effective hyperpolarizability.

The effect of the local field on the optical response of surfaces and thin films has been treated within the classical dipole model of polarizability [7, 9, 13, 14]. A point dipole model was used by Bagchi *et al* [9] to find the effective linear polarizabilities of adsorbed molecules, and this was extended to second-order non-linear polarizabilities by Ye and Shen [7]. Within this model, the x , y and z components of the local-field correction factor are given by (z normal to the surface)

$$L_{xx}(\omega) = L_{yy}(\omega) = [1 + (\alpha_{xx}(\omega)/2a^3)(\xi_0 - \rho(\omega)\xi_1)]^{-1} \quad (6)$$

$$L_{zz}(\omega) = [1 - (\alpha_{zz}(\omega)/2a^3)(\xi_0 + \rho(\omega)\xi_1)]^{-1}$$

with $\xi_0 = -9.0336$, $\rho(\omega) = (\epsilon_g - 1)/(\epsilon_g + 1)$, and

$$\xi_1 = 16\pi^2 \sum_{i=0}^{\infty} \sum_{j=1}^{\infty} (i^2 + j^2)^{1/2} \exp\left(-\frac{4\pi z_0}{a}(i^2 + j^2)^{1/2}\right)$$

where ϵ_g is the substrate dielectric function, $\alpha_{ii}(\omega)$ is the linear polarizability, a is the intermolecular separation of the active species, ξ_1 is the image dipole term, and z_0 is the distance of the molecule from the substrate. The symmetry of the susceptibility tensor is unchanged by the local field but the individual microscopic polarizabilities are modified by it. The effective hyperpolarizability in the laboratory frame is now

$$\beta_{ijk}^{\text{eff}} = L_{ii}(2\omega)L_{jj}(\omega)L_{kk}(\omega)\beta_{ijk} \quad (7)$$

with the L_{ii} being given by (6). When modified to incorporate the correction due to the local fields, and with the hyperpolarizability in the molecular frame, (2)–(4) become

$$\chi_{zzz} = N_s L_{zz}(2\omega)L_{zz}^2(\omega)\beta_{\zeta\zeta\zeta} \cos^3 \bar{\psi} \quad (8)$$

$$\chi_{zzy} = \frac{1}{2}N_s L_{zz}(2\omega)L_{yy}^2(\omega)\beta_{\zeta\zeta\zeta} \sin^2 \bar{\psi} \cos \bar{\psi} \quad (9)$$

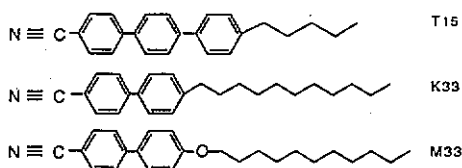
$$\tan^2 \bar{\psi} = [(L_{zz}(\omega)/L_{yy}(\omega))^2(2\chi_{zzy}/\chi_{zzz})]. \quad (10)$$

It is also useful to define an effective local-field correction factor in the z direction, from (8):

$$L_z^{\text{eff}} \equiv L_{zz}(2\omega)L_{zz}(\omega)^2 = \chi_{zzz}/N_s\beta_{\zeta\zeta\zeta} \cos^3 \bar{\psi}. \quad (11)$$

3. Experimental details

The molecules used are from the important class of substituted cyanobiphenyl and cyanoterphenyl thermotropic liquid crystals:



General aspects of the experiment have been described previously [10]. Briefly, ten good quality monolayers were prepared at room temperature on the triply distilled water subphase from solutions containing 0.01, 0.04, 0.09, 0.16, 0.25, 0.36, 0.49, 0.64, 0.81 and 1.00 mole fraction of the T15 liquid crystal in stearic acid, dissolved in chloroform. The monolayer films were transferred to a fused silica substrate at a dipping pressure of 35 mN m^{-1} , except for the 0.64, 0.81 and 1.00 mole fraction films where a lower dipping pressure of 12 mN m^{-1} was necessary to avoid collapse. Transfer ratios were above 0.95, indicating good quality films and allowing the accurate determination of the surface density of the molecules, N_s , on the substrate. Only one side of the substrate was coated in these experiments.

Linear optical absorption spectra could not be obtained from the monolayers, but fluorescence excitation spectra could be measured on a Perkin-Elmer MPF-44B spectrophotometer. The T15 liquid crystal and stearic acid mixed homogeneously in the monolayer, the evidence coming from isotherm measurements, the appearance of the Langmuir films on the subphase and the LB films on the fused silica substrate, and the absence of aggregation shifts in the optical spectra. Some segregation to domain boundaries cannot be ruled out, but for typical domain sizes in the μm régime, the small fraction of the molecules involved would not affect the SH response. In addition to the T15 films, 10% films of M33 and K33 were made, also at 35 mN m^{-1} dipping pressure. A 100% K33 film was prepared at 4.5 mN m^{-1} dipping pressure, but 100% M33 films could not be prepared, as discussed previously [10].

For the SHG experiments, a frequency-doubled Q-switched Nd/YAG laser, of pulse length 15 ns and 20 Hz repetition rate, was used to pump a dye laser for excitation at 628 nm. Laser pulse energy was maintained below 10 kJ m^{-2} to avoid any laser-induced desorption or damage effects. At these power densities no SHG was observed from either the substrate or pure stearic acid monolayers, and the SH intensity from the liquid crystal monolayers was typically a few photons per pulse, for measurements made in the transmission mode at 45° . For a linearly polarized incident wave at frequency ω and with the field vector making an angle α to the plane of incidence, the p and s components of the electric field of the transmitted SH wave are

$$E_{2\omega}^p(\alpha) = (A \cos^2 \alpha + B \sin^2 \alpha + C \sin 2\alpha) E_\omega(\alpha)^2 \quad (12)$$

$$E_{2\omega}^s(\alpha) = (F \cos^2 \alpha + G \sin^2 \alpha + H \sin 2\alpha) E_\omega(\alpha)^2 \quad (13)$$

where A to H depend on χ_{ijk} and the dielectric functions of the substrate and the monolayer film [10].

The dielectric function of the substrate is 2.122. For the monolayer, the dielectric function will, in general, be complex, $\epsilon = \epsilon' + i\epsilon''$. Values for stearic acid and T15 monolayers, at 632.8 nm, have been reported previously [10]. For stearic acid, the dielectric function is real in the frequency range of interest, $\epsilon' = 2.0(1)$, where the estimated error is given in parentheses. The dielectric function is also mostly real for T15 at the fundamental frequency, $\epsilon' = 2.3(1)$, $\epsilon'' = 0.3(1)$, but at the SH frequency, T15 is close to resonance. Recent surface plasmon polariton studies of dispersion in highly absorbing LB films show a variation of ϵ' , of +5% to -25% relative to the value at the long-wavelength side of the resonance, while ϵ'' varies from zero to 1.25 [15]. We use this behaviour to estimate that, for T15 around resonance, ϵ' lies between 1.8 and 2.3, and ϵ'' between 0.8 and 2.0. For mixed films, the dielectric function is found from the weighted average of the stearic acid and T15 values. This uncertainty in ϵ in the monolayer makes only a small contribution to the overall error, and this is included in the error estimates in figures 2-4, and table 1.

The SH intensity depends on the square of the field, $I(2\omega) \propto |E(2\omega)|^2$ and measurements are made of intensity as a function of polarization angle, α . Least-squares fitting of the variation of SH intensity as a function of α yields χ_{zzz} and χ_{zxy} . The SHG signal was calibrated by inserting an x-cut quartz plate in the input beam and observing the Maker fringes [16] produced by SHG in the bulk of the quartz, as described previously [17]. For quartz at 1064 nm excitation, $\chi_{xxx} = 6.4 (8) \times 10^{-13} \text{ mV}^{-1}$ [18]. Dispersion of the quartz SH response is neglected as all excitations in this study are well within the quartz band gap.

4. Results and discussion

Any local-field corrections due to the presence of the fatty acid will be small and can be neglected, because the correction factors arise from induced-dipole-induced-dipole interactions, and the dipole induced on the stearic acid is reduced by the ratio of linear polarizability, $\alpha_{\text{acid}}/\alpha_{\text{T15}}$, compared with that of the highly polarizable liquid crystal molecule.

The contrast between the local field in monolayers and the bulk local field can be seen by examining the behaviour of L_{ii} , for typical values of linear polarizabilities, as a function of surface density of active species on a glass substrate. Figure 1 shows the variation of L_{zz} , L_{xx} and L_{zz}/L_{xx} with surface density, calculated using (6). Although $L_{xx} \geq 1$, the intrinsic asymmetry at the surface gives $L_{zz} \leq 1$, in contrast to the bulk, isotropic local-field correction factor which is greater than one. For monolayer films, the local field opposes the component of the applied field in the z direction, thus *reducing* the effective field experienced by the molecule in this direction. For most LB monolayers, where the molecular distribution is uniaxial (isotropic in the plane) and the tilt angle is less than 90° , effective $\beta_{\zeta\zeta\zeta}$ values from concentrated films where the local field is important will be *reduced* from the isolated molecule value, in contrast to bulk material where effective $\beta_{\zeta\zeta\zeta}$ values are *increased* by the local-field effect.

Quantitative evaluation of local-field effects can be made using (8)–(11). These equations relate complex quantities, and it has been shown how SH phase measurements can be used to evaluate the real and imaginary parts of χ_{ijk} and $\beta_{\zeta\zeta\zeta}$ [10]. Here, results are analysed in terms of $|\chi_{ijk}|$ and $|\beta_{\zeta\zeta\zeta}|$, which are directly related to the SH intensity measurements. However, the main results reported are for T15, using 628 nm excitation, where there is the simplification that χ is imaginary, because the SH response is on resonance [10].

In the absence of local-field effects, (8) shows that a plot of $|\chi_{zzz}|/\cos^3\psi$ against N_s should be linear [4, 8] with a slope determined by $|\beta_{\zeta\zeta\zeta}|$. Deviations from linearity at higher N_s values can then be used to evaluate L_z^{eff} in (11). As has been pointed out by Hayden [8], the problem in this approach is that, as shown by (10), local fields also affect the determination of the tilt angle ψ , and it is clear from the L_{zz}/L_{xx} plot in figure 1, that the effect could be significant at large tilt angles. For the T15 films prepared under the conditions described above, the tilt angle is zero, within experimental error, except for the 0.64, 0.81 and 1.00 mole fraction films. Uncorrected for the local-field effects, values of ψ of 68° , 75° and 76° , respectively, are obtained for these fractions. For reasonable estimates of the unknown parameters in (6), α_{ii} and z_0 , the angles become $49(5)^\circ$, $52(5)^\circ$ and $53(5)^\circ$, respectively, with estimated errors in parentheses, and the evaluation of L_z^{eff} may now proceed. We note in passing that, under these conditions, there are only two preferred angles for the T15 molecules in T15–stearic acid mixtures, $\simeq 0^\circ$ and $\simeq 50^\circ$, corresponding to the two dipping pressures of 35 mN m^{-1} and 12 mN m^{-1} . This only becomes apparent when local-field effects are taken into account.

Figure 2 shows a plot of $|\chi_{zzz}|/\cos^3\bar{\psi}$ against N_s , with $\bar{\psi}$ for the last three points corrected as described above, for 628 nm excitation. The error bars incorporate both experimental errors and uncertainty in the dielectric constants of the monolayer film. The departure from linearity becomes significant around 0.2 mole fraction of T15, corresponding to a molecular separation of 11 Å. The straight line in figure 2 represents a least-squares fit to the data from the dilute mixtures (0.01, 0.04, 0.09, 0.16), where local-field effects are negligible. The slope of the line is used to determine $|\beta_{\zeta\zeta\zeta}|$, which then allows the local-field correction factors in the more concentrated mixtures to be found.

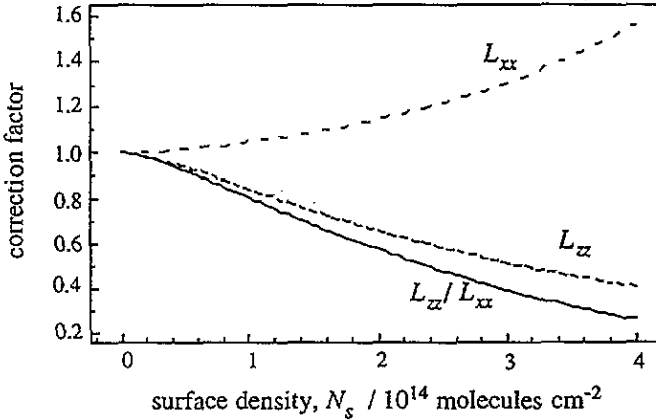


Figure 1. Plot of local-field correction factors as a function of surface density, for the following parameter values: $\alpha_{xx}(\omega) = 10 \text{ \AA}^3$, $\alpha_{zz}(\omega) = 20 \text{ \AA}^3$, $z_0 = 5 \text{ \AA}$, $\epsilon_z = 2.2$, and $a = 1/\sqrt{N_s}$.

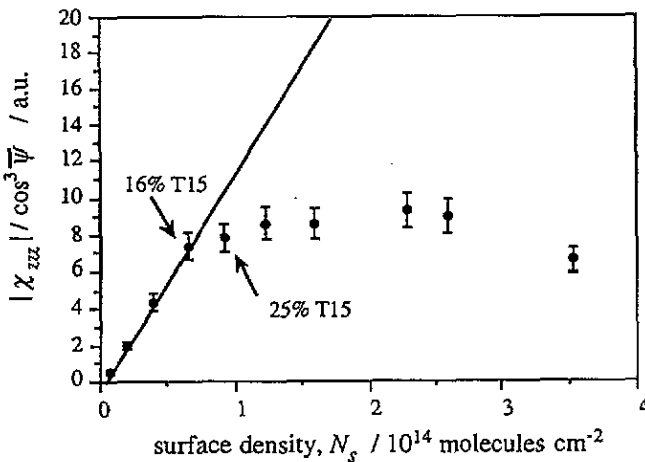


Figure 2. Plot of $|\chi_{zzz}|/\cos^3\bar{\psi}$ against N_s the surface density of the T15 molecule on the fused silica substrate, for 628 nm excitation. 0.25 mole fraction of T15 corresponds to a molecular separation of about 13 Å. The error bars in the figure include both experimental errors and the uncertainty in the choice of the linear dielectric constants for the monolayer.

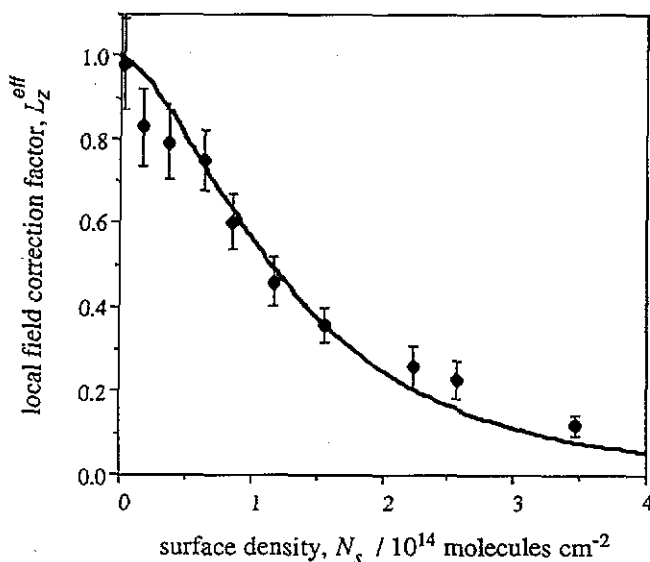


Figure 3. Effective local-field correction factor normal to the substrate surface, L_z^{eff} , as a function of the surface density, N_s .

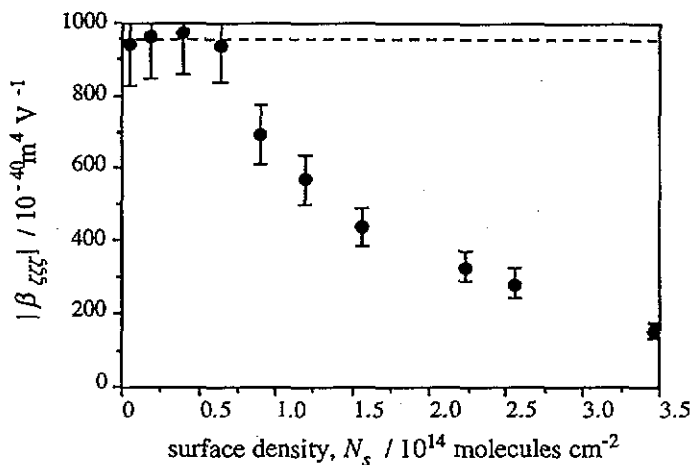


Figure 4. Variation of effective value of $|\beta_{zzz}|$ with surface density, N_s . The horizontal dashed line corresponds to no local-field effect.

Figure 3 shows the experimentally determined local-field correction factor, L_z^{eff} , as defined in (11). Much less scatter is seen in the results of figure 3 than in the previous study of hemicyanine [8], due to improved data and, perhaps, the absence of aggregation effects in the T15 system. The theoretical curve from (6) is also shown in the figure. The theoretical parameters are the substrate dielectric function, the intermolecular separation $a = 1/\sqrt{N_s}$, where N_s is the surface density of T15 molecules, the chromophore-substrate separation, z_0 , and the linear polarizability $\alpha_{zz}(\omega)$. z_0 was set equal to $z \cos \bar{\psi}$, where z is the linear distance from the substrate end of T15 molecule to the centre of the π electron

cloud (taken as 10 \AA [19]). The combination of the large z_0 value of the T15 molecule and the small dielectric function of the substrate makes the image dipole contribution very small. In the absence of measurements of α_{zz} at ω and 2ω for the T15 monolayer, these parameters were allowed to vary to obtain the best non-linear least-squares fit to the experimental data, and the solid line in figure 3 corresponds to $\alpha_{zz}(\omega) = 20 \text{ \AA}^3$ and $\alpha_{zz}(2\omega) = 29 \text{ \AA}^3$. While $\alpha_{zz}(2\omega)$ will be larger than $\alpha_{zz}(\omega)$ because the SH frequency is near resonance for T15, the value of $\alpha_{zz}(\omega)$ is smaller than expected from bond additivity. Each phenyl group should contribute 10 \AA^3 to $\alpha_{zz}(\omega)$ [20], producing a value of at least 30 \AA^3 for the T15 molecule. It is probable that the fitting procedure is disguising the limitations of the simple theory.

Limitations of the model have been discussed by Hayden [8]. In particular, the model applies to point dipoles, but the dipoles induced in the adsorbed molecules can only be treated as points when the spatial extent of the dipole is much less than the separation between the molecules. This condition is true only for dilute mixtures of T15 and stearic acid. For example, even in mixtures where the T15 mole fraction is 0.04, the intermolecular separation is $\simeq 25 \text{ \AA}$ and thus only about three times larger than the spatial extent of the dipole. Also, the theory applies to adsorbed molecules perpendicular to the substrate surface, and the T15 molecules tilt away from the surface normal for 0.64 mole fraction and above.

We can now explain the drop in the apparent value of $|\beta_{\zeta\zeta\zeta}|$ determined from the SH measurements. This is shown in figure 4. For dilute monolayers (0.01, 0.04, 0.09 and 0.16 mole fraction), $|\beta_{\zeta\zeta\zeta}|$ is constant. The $|\beta_{\zeta\zeta\zeta}|$ value drops for higher concentrations and, for the pure T15 monolayer, has dropped by a factor of six. The $|\beta_{\zeta\zeta\zeta}|$ values for condensed organic thin films without local-field correction, quoted by many workers, must be smaller than the $|\beta_{\zeta\zeta\zeta}|$ value for the isolated molecule. The discrepancy is even greater if the bulk isotropic correction factor is applied in an attempt to estimate an isolated molecule value, as this decreases $|\beta_{\zeta\zeta\zeta}|$ further.

Resonance enhancement of the SH signal may also change the $|\beta_{\zeta\zeta\zeta}|$ value. Table 1 summarizes $|\beta_{\zeta\zeta\zeta}|$ values for three liquid crystal molecules at two different wavelengths and concentrations. In determining these values, the local-field correction to the tilt angle of T15 has been applied to K33 and M33, a reasonable procedure given the similarity of the molecular structures. The $|\beta_{\zeta\zeta\zeta}|$ value for pure K33 using 532 nm excitation, $109(15) \times 10^{-40} \text{ m}^4 \text{ V}^{-1}$, increases to $160(20) \times 10^{-40} \text{ m}^4 \text{ V}^{-1}$ if the tilt angle is not corrected for local-field effects. Previous work has reported a $|\beta_{\zeta\zeta\zeta}|$ value of $105 \times 10^{-40} \text{ m}^4 \text{ V}^{-1}$ for this molecule, uncorrected for local-field effects [4]. The table shows a wavelength dependence of the results for the three molecules, which is consistent with resonances at 325 nm, 305 nm and 295 nm, for T15, M33 and K33, respectively [10], and which supports the view that the non-linear optical response of this class of thermotropic liquid crystals, in general, will be similar to T15.

Table 1. Effective $|\beta_{\zeta\zeta\zeta}|$ values for three liquid crystal molecules under different LB monolayer preparation conditions. The dipping pressure is 12 mN m^{-1} for 100% T15, 4.5 mN m^{-1} for 100% K33, and 35 mN m^{-1} for all the 10% samples. These conditions give a corrected tilt angle, $\psi = 53(5)^\circ$ for 100% T15, $66(7)^\circ$ for 100% K33, and $0(3)^\circ$ for all the 10% samples. Estimated errors are given in parentheses.

$ \beta_{\zeta\zeta\zeta} /10^{-40} \text{ m}^4 \text{ V}^{-1}$ SH wavelength	10% mol		100% mol	
	314 nm	266 nm	314 nm	266 nm
T15	980(130)	480(60)	160(20)	65(9)
M33	900(120)	710(90)	—	—
K33	380(50)	840(110)	46(6)	109(15)

Both the local-field effect and the presence of resonances must be considered when determining the true $\beta_{\xi\eta\zeta}$ values of an isolated organic molecule. For T15, the resonant $|\beta_{\xi\zeta\xi}|$ value for the diluted monolayer is about fifteen times greater than the non-resonance value for the concentrated monolayer. These two factors must be taken into account if comparison with theoretical $\beta_{\xi\eta\zeta}$ values is to be made.

5. Conclusion

The concentration dependence of the SH response of mixed liquid crystal-stearic acid LB monolayers has been studied. The local field was confirmed to be a major factor in the concentration dependence of the SHG response. The determination of both molecular orientation and $\beta_{\xi\eta\zeta}$ values is effected by the local field. The separation at which the induced-dipole-induced-dipole interaction of T15 molecules in a mixed T15-stearic acid monolayer becomes significant is about 11 Å. It is recommended that, when LB monolayers are being used to determine the molecular $\beta_{\xi\eta\zeta}$ values, the active molecules should be diluted by about a factor of ten in inactive buffer molecules. With the quality of data it is now possible to obtain, more sophisticated modelling of the local-field effect should be attempted, even though the results presented here could be fitted quite well to the point dipole model by allowing the linear polarizability to assume a smaller than expected value. These LB monolayers are ideal model systems for testing theoretical approaches to the local-field problem, and progress in this area is important in understanding the optical response of surfaces and interfaces in general, and those of semiconductors in particular [3, 13, 14]. In addition, the local-field effect is an important consideration in the design of materials for ultra-thin-film non-linear optical devices.

Acknowledgments

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