An SHG Magic Angle: Dependence of Second Harmonic Generation Orientation Measurements on the Width of the Orientation Distribution

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Received October 21, 1998

The existence of a "magic angle" in molecular orientation determined by second harmonic generation (SHG) is reported. The magic angle is predicted from Legendre polynomial expansion of a distribution in molecular orientation angles. Sufficiently broad molecular distributions yield an apparent molecular tilt angle of 39.2°, regardless of the true distribution mean.

SHG is a well-established and widely used method for probing molecular orientation at surfaces and interfaces, by nature of its inherent interface selectivity and wide applicability. By comparing the relative intensities of second harmonic light generated under different polarization conditions for both the fundamental and the second harmonic, it is possible to determine the mean tilt angle of surface species. For a uniaxial system comprised of rod-like molecules with a single dominant component of the molecular second order polarizability tensor lying along the long molecular axis (in other cases, D can be related to different combinations of tensor elements), the molecular tilt angle can be calculated using the following relation:[1,2]

$$D \equiv \frac{\langle \cos^3 \theta \rangle}{\langle \cos \theta \rangle} = \frac{\chi^{(2)}_{zzz}}{\chi^{(2)}_{zzz} + 2\chi^{(2)}_{zxx}} \cong \cos^2\langle \theta \rangle \qquad (1)$$

in which D is an orientation parameter, θ is the tilt angle of the molecular long axis with respect to the orientation axis, $\chi^{(2)}$ is a nonlinear susceptibility tensor, and the brackets indicate an expectation value. The first subscript indicates the direction of nonlinear polarization within the interfacial layer when driven by electric field components polarized in the directions indicated by the second and third subscripts. The relative magnitude of each tensor element is proportional to the square root of the SHG intensity measured under the appropriate polarization conditions after correcting for the blank response, local field factors, and Fresnel factors.[3−5]

The approximation given in eq 1, in which $D \cong \cos^2\langle\theta\rangle$, is valid if the distribution about the mean tilt angle is narrow, such that a δ-function may be substituted for the distribution function. However, in many instances, the widely used δ-function approximation may not be justifiable. With the possible exception of tightly packed monolayer films, it is reasonable to expect some distribution about the mean molecular tilt angle.[6,7] Additionally, there is compelling evidence from work performed in our laboratory[8,9] and in others laboratories[10−14] that surface and interface roughness can significantly broaden the orientation distribution, such that the δ-function approximation is quite poor.

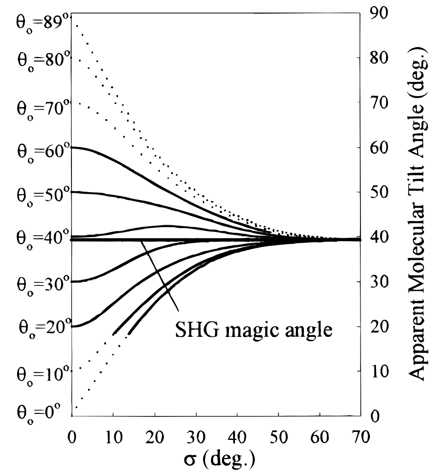

Figure 1. The apparent molecular tilt angle (calculated by incorrectly assuming a δ-function distribution, as in eq 1) as a function of the root-mean-square width (σ) of a Gaussian distribution. Each curve corresponds to a different distribution mean (θ_o). The straight line at 39.2° is the SHG magic angle. Dotted portions of the curves indicate regions in which either $\langle\cos^3 \theta\rangle$ or $\langle\cos \theta\rangle$ drops below 0.1 of the maximal value, corresponding to an SHG intensity approximately 1% of maximum (maximal value = evaluated at $\theta_o = 0$, $\sigma = 0$).

To probe the dependence of the SHG response on the width of an orientation distribution, calculations were performed using a Gaussian distribution, where the width of the distribution is represented by σ. The same net results were obtained using either a Gaussian distribution in which all contributions were summed into the interval from 0 to π, a Gaussian distribution truncated at 0 and π, or a Lorentzian distribution. The validity of each distribution used in SHG calculations was first tested by verifying that the asymptotic limit of a broad distribution yielded an apparent tilt angle for linear dichroism (LD) equal to 54.7° (i.e., the LD magic angle). Since linear dichroism orientation measurements are dependent on $\langle\cos^2 \theta\rangle$, the observed convergence to the LD magic angle for broad distributions provides strong evidence that SHG orientation calculations based on $\langle\cos \theta\rangle$ and $\langle\cos^3 \theta\rangle$ using the same distribution functions are also reliable. Further details regarding the distribution functions are provided in the Supporting Information.

The influence of varying the width of the distribution on the apparent tilt angle determined by SHG is shown in Figure 1. The apparent tilt angle is defined to be the angle calculated using the δ-function approximation (which is the assumption most often made in SHG orientation investigations). Dotted portions of the curves indicate regions in which either $\chi^{(2)}_{zzz}$ or $\chi^{(2)}_{zxx}$ drops below 0.1 of its maximal value; i.e., the dotted portions indicate regions in which the signal-to-noise ratio is likely to prohibit accurate orientation measurements. As expected, for narrow distributions the apparent tilt angle corresponds well with the true mean of the Gaussian distribution. However, in cases in which the distribution is not narrow, significant deviation can occur between the true mean and the mean calculated by incorrectly assuming a δ-function distribution. Two aspects of Figure 1 are particularly intriguing: (1) all curves converge to an apparent tilt angle of 39.2° regardless of the true distribution mean, and (2) the convergence to 39.2° occurs more quickly than the overall loss of SHG intensity, which suggests that the convergence may be observed experimentally.

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10.1021/ja983683f CCC: $18.00
Published on Web 03/06/1999

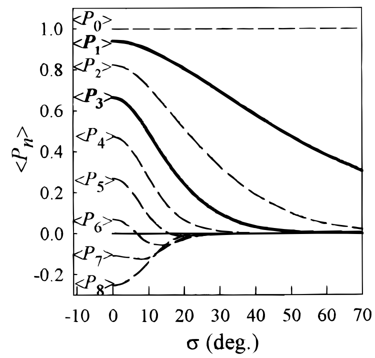

Figure 2. The first eight Legendre moments of a Gaussian distribution centered at 20° are shown as the distribution is broadened. Solid lines indicate the first and third Legendre moments.

The convergence to 39.2°, a magic angle, can be explained using Legendre polynomials to relate the orientation parameter D to the width of the orientation distribution. By rewriting the expectation values given in eq 1 in terms of Legendre polynomials, the parameter D can be written as a function of only the first and third Legendre moments (a Legendre moment is defined to be the expectation value of a Legendre polynomial)

$$D \equiv \frac{\langle \cos^3 \theta \rangle}{\langle \cos \theta \rangle} = \frac{{}^2/_5 \langle P_3 \rangle + {}^3/_5 \langle P_1 \rangle}{\langle P_1 \rangle} \tag{2}$$

Here $\langle P_n \rangle$ is an abbreviation for $\langle P_n(\cos \theta) \rangle$, where P_1 equals cos θ and P_3 equals $(5 \cos^3 \theta - 3 \cos \theta)/2$. The dependence of $\langle P_1 \rangle$ and $\langle P_3 \rangle$ on the width of the molecular distribution function can be clarified by expanding the distribution function in an infinite series of Legendre polynomials[15]

$$f(\theta) = \sum_{n=0}^{\infty} \left(\frac{2n+1}{2} \right) \langle P_n \rangle P_n \tag{3}$$

in which $f(\theta)$ is the distribution function. Each expansion coefficient is proportional to the corresponding Legendre moment. Therefore, knowledge of all the Legendre moments allows for complete reconstruction of the distribution function. Each Legendre moment is given by[15]

$$\langle P_n \rangle = \int_{-1}^{1} f(\theta) P_n \mathrm{d} \cos \theta = \int_0^{\pi} f(\theta) P_n \sin \theta \, \mathrm{d}\theta \tag{4}$$

Using eq 4, the first few Legendre moments of a Gaussian distribution were calculated for a mean tilt angle of 20° (arbitrarily chosen). The results of the calculations as a function of the distribution width (σ) are shown in Figure 2. From the figure, it is clear that the higher order Legendre moments systematically approach zero faster than the lower moments as the distribution is broadened. Similar trends were observed for all mean tilt angles analyzed (ranging from 0 to 89°), for both Gaussian and Lorentzian distributions. Specifically, the more rapid approach of $\langle P_3 \rangle$ to zero compared with $\langle P_1 \rangle$ offers an explanation for the apparent tilt angle convergence observed in Figure 1. In the limit of $\langle P_3 \rangle$ being much smaller than $\langle P_1 \rangle$, the parameter D becomes independent of the distribution function, approximately equal to a constant of ${}^3/_5$. If a narrow distribution is incorrectly assumed in this case, the tilt angle calculated using eq 1 will be equal to the SHG magic angle, 39.2° (i.e., $39.2° = \cos^{-1}[({}^3/_5)^{1/2}]$).

The sequential loss of higher order Legendre moments predicts a specific sequence of events to be observed as the distribution broadens; the apparent tilt angle as determined from SHG measurements should converge to the magic angle (corresponding to $\langle P_3 \rangle$ approaching zero), followed by loss of linear dichroism and birefringence (corresponding to $\langle P_2 \rangle$ approaching zero), and eventually loss of all SHG (corresponding to $\langle P_1 \rangle$ approaching zero). In fact, a number of experimental investigations have reported observation of SHG but an absence of phenomena related to $\langle P_2 \rangle$ (such as linear dichroism and birefringence). Wang et al. demonstrated experimentally that SHG can occur in systems which do not exhibit birefringence.[16] Additionally, in a surface multilayer film containing azo dye chromophores, Katz and coworkers reported SHG, although no linear dichroism was observed.[17,18]

Compelling theoretical and experimental evidence for the existence of the SHG magic angle can also be found from studies of poled polymer films. In poled polymer relaxation studies conducted by Song et al., linear dichroism was observed to approach its isotropic value much more quickly than loss in SHG intensity upon removal of an orienting poling field.[19] Although the trends observed by Song et al. were explained by coherence effects and trapped charges, an alternative explanation is that the orientation distribution, which is relatively broad under normal poling conditions (i.e., $\langle P_3 \rangle$ is essentially zero), broadened further upon relaxation, resulting in $\langle P_2 \rangle$ approaching zero followed by $\langle P_1 \rangle$ approaching zero.

In theoretical treatments of orientation in poled polymer films, expansion of a Gibbs distribution in terms of Langevin functions in the limit of a weak applied field (and correspondingly a broad distribution) leads to the following relationship between $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$:[20,21]

$$\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz} = {}^1/_3 \tag{5}$$

The one-to-three relationship between the two tensor elements has been found to hold true experimentally under most reasonable poling conditions with only a few exceptions.[21] If we substitute the relationship shown in eq 5 into eq 1, D is again equal to ${}^3/_5$, yielding the SHG magic angle result from an entirely different mathematical approach.

On the basis of the existence of a magic angle in SHG, the use of SHG for orientation measurements should be carefully evaluated. For example, in a cursory search we identified 19 publications, spanning over 15 years, which reported molecular tilt angles (determined by SHG) of 39 (±2°). If the choice of a narrow distribution is not justifiable, the measured mean tilt angles could be inaccurate. Even in cases in which the SHG magic angle is not observed, assuming a narrow distribution erroneously could result in a calculated mean tilt angle significantly different from the true mean tilt angle.

Acknowledgment. The authors gratefully acknowledge funding from the National Science Foundation.

Supporting Information Available: A description of the distribution functions used in calculations, and a list of publications citing orientation angles by SHG within 2° of 39° (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA983683F

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