PHYSICAL REVIEW E VOLUME 57, NUMBER 6 JUNE 1998

Determination of orientational distribution function of organic molecular surfaces using the modified maximum-entropy method

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(Received 26 November 1997)

The determination of the surface orientational distribution function for organic molecules such as liquid crystals has been studied using the maximum-entropy method with second-order optical nonlinear coefficients. Systematic simulation revealed that the conventional maximum-entropy method does not give sufficient information about the axial ordering ($\langle\cos^2\theta\rangle$) along the surface normal direction (θ is the angle between the molecular axis and surface normal direction). We propose a modified maximum-entropy method that involves an additional constraint function of $\langle\cos^2\theta\rangle$ and gives more realistic distribution functions. Distribution functions were determined for several previous experimental results using these conventional and modified methods. From the comparison of these distribution functions, it has been shown that the distribution densities of molecules oriented at tilt angle $\theta=180°$, which appear when using the conventional maximum-entropy method, are artifacts. [S1063-651X(98)04606-6]

PACS number(s): 61.30.−v, 68.45.−v, 64.70.−p, 42.65.Ky

I. INTRODUCTION

The understanding of the orientational distribution of organic systems at a surface or an interface is not only of fundamental interest but also of practical importance for designing and constructing organic devices such as liquid-crystal (LC) displays [1–9]. In the past few years, many kinds of optical methods have been used in order to obtain information about surface orientation [10–12]. Among them, optical second-harmonic generation (SHG) has proved to be an effective tool for studying the alignment or arrangement of adsorbed molecular monolayers [12–14]. Using this technique, one can deduce the orientational distribution function of molecules from the second-order nonlinear optical (NLO) coefficients.

Previously, several models have been proposed to obtain information about the orientational distribution. As for the systems of $C_{\infty v}$, we can obtain the average tilt (polar) angle θ_0 of the molecules at the monolayer surface from the ratio of the two nonvanishing NLO coefficients [12–17]. For the determination, however, a Gaussian distribution of a certain width must be assumed. Hence the average orientation was usually determined by assuming a sharp (δ-functional) distribution. Recently, Yoo *et al.* proposed a method to determine the unbiased distribution function in the system of $C_{\infty v}$ symmetry [18].

As for the systems of C_{1v} symmetry, two models were adopted. In the first model, one neglects the dependence of θ on the azimuthal angle ϕ and assumes the distribution function

$$f(\theta,\phi)=C_1\exp[-(\theta-\theta_0)^2/2\sigma^2][1+d_1\cos\phi+d_2\cos2\phi+d_3\cos3\phi], \tag{1}$$

where C_1 is the normalization constant and σ the width of θ distribution. Therefore, the distribution with a uniform average polar angle and a biased distribution along the azimuth angle is obtained using this model [1–5]. The second model is the maximum-entropy method. This method is a method of ‘‘reasoning’’ developed in the field of information theory [19]. The basic concept is to determine a solution using known information under the least bias for unknown information. For this purpose, the concept of information entropy is introduced to deal with any incompleteness and the information entropy is maximized under constraints. This method has been widely used in data analysis of various experiments such as x-ray and neutron diffraction for determining the electron and nuclear densities [20,21] and polarized fluorescence [22] and Raman [23] measurements for determining molecular orientational distributions. In the present work we apply this method to SHG data and obtain the unbiased orientational distribution of a molecular monolayer [6,7]. Up to now this method has been widely applied to obtain the orientational distributions of various kinds of organic systems such as LC monolayers [6–9], side-chain polymer surfaces [7,24], and polymer monolayers [25]. However, using this method, unrealistic distributions have sometimes been deduced, i.e., a relatively high distribution peak at a molecular tilt angle of 180° [6,9]. This peak could be interpreted as the distribution density for molecules with their polar end group away from the substrate surface [6,9]. However, the deduced distribution may not be a real distribution function because the proportion of peaks at $\theta=180°$ is too high, namely, over 15–25 % with respect to the main distribution peak [6,9].

In this paper the procedure for determining orientational distribution functions is examined using the maximum-entropy method with second-order optical nonlinear coefficients. According to systematic simulation, we point out problems in the conventional maximum-entropy method and propose a modified method to avoid errors leading to more accurate information about the molecular distribution at surface. Then the adequacy of this method is exemplified by determining several distribution functions using the modified method with second-order NLO results reported previously [1,2,9,18].

II. THEORETICAL BACKGROUND

First, a brief review is given of the determination of the orientational distribution of molecules from surface SHG data since the theory of surface SHG from adsorbed monolayers has already been described in detail elsewhere [12–14]. The intensity of SHG light $I(2\omega)$ from a monolayer sample is given by

$$I(2\omega)\propto|\chi_{eff}^{(2)}|^2 I^2(\omega), \tag{2}$$

where $I(\omega)$ is the fundamental beam intensity. $\chi_{eff}^{(2)}$ is the effective nonlinear susceptibility of the surface and is defined by

$$\chi_{eff}^{(2)}=[\hat{e}(2\omega)\cdot L(2\omega)]\chi^{(2)}:[L(\omega)\cdot\hat{e}(\omega)][L(\omega)\cdot\hat{e}(\omega)], \tag{3}$$

where $\chi^{(2)}$ is a second-order nonlinear susceptibility tensor, $\hat{e}(\Omega)$'s are unit polarization vectors at frequency Ω, and $L(\Omega)$'s are macroscopic local-field factor (or Fresnel factor) tensors.

For a rodlike adsorbed molecule, the second-order hyperpolarizability is dominated by a single element $\beta_{\xi\xi\xi}$ along the molecular long axis ξ [12–14]. The monolayer of such molecules on the surface has a nonlinear susceptibility tensor $\chi^{(2)}$ given by

$$\chi_{ijk}^{(2)}=N_s\langle(\hat{i}\cdot\hat{\xi})(\hat{j}\cdot\hat{\xi})(\hat{k}\cdot\hat{\xi})\rangle\beta_{\xi\xi\xi}^{(2)}, \tag{4}$$

where N_s is the surface molecular density and $(\hat{i},\hat{j},\hat{k})$ refers to the unit vectors of the sample coordinates (x,y,z), where z is the direction of the surface normal. The angular bracket denote the orientational average weighted by a distribution function $f(\theta,\phi)$ of molecules. An ensemble of rodlike molecules can be described in terms of a $\chi^{(2)}$ tensor by just six independent components in C_{1v} symmetry [6]:

$$\begin{aligned}
\chi_1&=\chi_{zzz}=N_s\langle\cos^3\theta\rangle\beta_{\xi\xi\xi}^{(2)},\\
\chi_2&=\chi_{xxx}=N_s\langle\sin^3\theta\cos^3\phi\rangle\beta_{\xi\xi\xi}^{(2)},\\
\chi_3&=\chi_{zyy}=\chi_{yzy}=\chi_{yyz}\\
&=N_s\langle(\cos\theta-\cos^3\theta)\rangle\langle(1-\cos^2\phi)\rangle\beta_{\xi\xi\xi}^{(2)},\\
\chi_4&=\chi_{zxx}=\chi_{xzx}=\chi_{xxz}=N_s\langle(\cos\theta-\cos^3\theta)\rangle\langle\cos^2\phi\rangle\beta_{\xi\xi\xi}^{(2)},\\
\chi_5&=\chi_{zxz}=\chi_{zzx}=\chi_{xzz}=N_s\langle(\sin\theta-\sin^3\theta)\rangle\langle\cos\phi\rangle\beta_{\xi\xi\xi}^{(2)},\\
\chi_6&=\chi_{xyy}=\chi_{yxy}=\chi_{yyx}=N_s\langle\sin^3\theta\rangle\langle(\cos\phi-\cos^3\phi)\rangle\beta_{\xi\xi\xi}^{(2)},
\end{aligned} \tag{5}$$

where θ is the polar angle between the molecular axis ξ and the sample coordinate z axis and ϕ is the azimuthal angle between ξ and x axes. In the case of azimuthal isotropy ($C_{\infty v}$ symmetry) $\langle\cos^n\phi\rangle=0$ when n is odd and $\langle\cos^2\phi\rangle=\langle 1-\cos^2\phi\rangle=1/2$. Hence Eq. (5) reduces to just two independent nonvanishing elements $\chi_{zzz}^{(2)}$ and $\chi_{zxx}^{(2)}$.

By measuring surface SHG as a function of rotation angle Φ about its surface normal direction for different input and output polarization combinations, i.e., p in and p out, s in and p out, s in and s out, and p in and s out, the values of $\chi_{ijk}^{(2)}$ can be deduced using Eqs. (2)–(5). From these values of $\chi_{ijk}^{(2)}$, we can obtain information about the orientational distribution function of the monolayer on the surface. In order to obtain an ''unbiased'' estimate of the orientational distribution function, we have used the maximum-entropy method [6,7]. This provides a constructive method for obtaining distributions on the basis of partial knowledge. In this method, information is the average value of the following constraint functions obtained from the measurements of $\chi^{(2)}$:

$$\begin{aligned}
f_1(\theta,\phi)&=\cos^3\theta,\\
f_2(\theta,\phi)&=\sin^3\theta\cos^3\phi,\\
f_3(\theta,\phi)&=(\cos\theta-\cos^3\theta)(1-\cos^2\phi),\\
f_4(\theta,\phi)&=(\cos\theta-\cos^3\theta)\cos^2\phi,\\
f_5(\theta,\phi)&=(\sin\theta-\sin^3\theta)\cos\phi,\\
f_6(\theta,\phi)&=\sin^3\theta(\cos\phi-\cos^3\phi).
\end{aligned} \tag{6}$$

In order not to introduce any bias, we need to maximize the uncertainty on the distribution function defined by

$$H(f(\theta,\phi))=-\int_0^{\pi}\sin\theta\,d\theta\int_0^{2\pi}f(\theta,\phi)\ln f(\theta,\phi)d\phi \tag{7}$$

under the constraints using the six Lagrange undetermined multipliers λ_i. This is equivalent to maximizing the quantity $H-\Sigma\lambda_i f_i$ and maximization leads to the distribution function

$$f(\theta,\phi)=\frac{\exp[\Sigma\lambda_i f_i(\theta,\phi)]}{\int_0^{2\pi}\int_0^{\pi}\exp[\Sigma\lambda_i f_i(\theta,\phi)]\sin\theta\,d\theta\,d\phi}. \tag{8}$$

Here λ_i's ($i=1$–6) can be calculated from the set of equations

$$\langle f_i(\theta,\phi)\rangle=\int_0^{2\pi}\int_0^{\pi}f_i(\theta,\phi)f(\theta,\phi)\sin\theta\,d\theta\,d\phi. \tag{9}$$

This method gives the widest distribution compatible with available information on $f(\theta,\phi)$.

III. MODIFIED MAXIMUM-ENTROPY METHOD

A. Estimation of the maximum-entropy method

In order to judge whether the method is appropriate for the determination of the orientational distribution functions, the maximum-entropy method was estimated. The procedure is as follows. First, a certain distribution function f is assumed. Then we can determine the average values of the parameters $f_i(\theta,\phi)$ using Eq. (9). These parameters are responsible for the nonlinear coefficients for Eqs. (5) and (6). From the six constraint functions with these values of the parameters, another orientational distribution function f' can be deduced using the maximum-entropy method. By comparing the original distribution f with the deduced distribution f', the method can be judged as to whether it is appropriate for the determination of the orientational distribution.

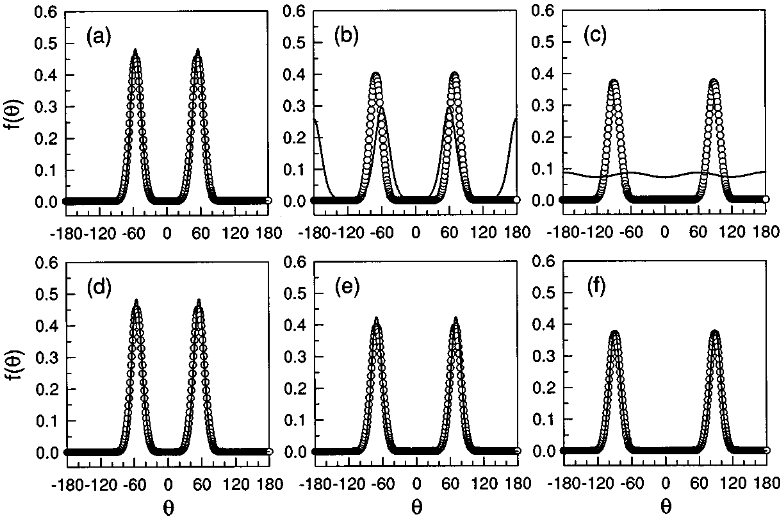

FIG. 1. Orientational distribution functions as a function of tilt angle θ_0. θ is the tilt angle (degree). Open circles represent the original Gaussian functions f and lines denote the deduced functions f' and f'' determined using the conventional and the modified maximum-entropy methods, respectively: (a) f and f' for $\theta_0=55°$, (b) f and f' for $\theta_0=70°$, (c) f and f' for $\theta_0=89°$, (d) f and f'' for $\theta_0=55°$, (e) f and f'' for $\theta_0=70°$, and (f) f and f'' for $\theta_0=89°$.

Let us first consider a system of $C_{\infty v}$ symmetry. As a test distribution function f we assume a Gaussian distribution with an average tilt angle θ_0 and a width σ,

$$f=C_2\exp[-(\theta-\theta_0)^2/2\sigma^2], \tag{10}$$

where C_2 is the normalization constant. In this case, the distribution is azimuthally isotropic ($C_{\infty v}$); thus there are only two nonvanishing constraint functions $\cos^3\theta$ and $(\cos\theta-\cos^3\theta)/2$, which are responsible for χ_{zzz} and χ_{zxx}, respectively. We calculated $\langle\cos^3\theta\rangle$ and $\langle\cos\theta-\cos^3\theta\rangle/2$ values using Eqs. (9) and (10) with various θ_0's and a fixed σ of 10°. These results provide constraints in addition to four other zero χ_{ijk}'s for the maximum-entropy method and lead to an orientational distribution function f'. Then the original distribution function f was compared with the deduced distribution f' for various θ_0's. These results are shown in Figs. 1(a), 1(b), and 1(c), where $\theta_0=55°$, 70°, and 89°, respectively. In the figures the original distributions (f) are plotted with open circles and the deduced distributions (f') are shown as solid lines.

For the case whose θ_0 is less than 55°, it was found that the deduced distribution f' is identical to the original Gaussian distribution f within the calculation error band. One of the examples is shown in Fig. 1(a) ($\theta_0=55°$, $\sigma=10°$), where perfect agreement is seen between the deduced f' (solid line) and the original f (open circle). However, when θ_0 is larger than 55°, the deduced distribution f' does not coincide with the original distribution f, as shown in Figs. 1(b) and 1(c). The disagreement becomes greater with increasing θ_0. It should be noted that the distribution density in the deduced f' is not zero when θ is near 180°, whereas that in the original distribution f is zero. Thus this analysis clearly shows that the conventional maximum-entropy method brings about an erroneous orientational distribution if θ_0 is larger than 55°.

The tilt angle of 55°, more precisely 54.7°, is known as a magic angle θ_m, defined by $3\cos^2\theta_m-1=0$. Hence the disagreement for $\theta_0>55°$ mentioned above must be physically accountable. In order to find the meaning of this angle, the average values of three parameters $\cos^3\theta$, $\cos\theta$, and $\cos^2\theta$ were monitored as a function of θ_0. Table I lists the calculated average values of these parameters for the original distribution f and the deduced distribution f'. As shown in the table, the average values of $\cos\theta$ and $\cos^3\theta$ for the deduced

TABLE I. Calculated average values of $\cos^3\theta$, $\cos\theta$, and $\cos^2\theta$ for the original Gaussian distribution function (GF), the deduced distribution determined using the conventional maximum-entropy method (ME), and the deduced distribution determined using the modified maximum-entropy method (MM) as a function of molecular average tilt angle θ_0.

	GF			ME			MM		
θ_0	$\cos^3\theta$	$\cos\theta$	$\cos^2\theta$	$\cos^3\theta$	$\cos\theta$	$\cos^2\theta$	$\cos^3\theta$	$\cos\theta$	$\cos^2\theta$
0	0.915	0.027	0.942	0.916	0.027	0.942	0.915	0.027	0.941
10	0.847	0.048	0.893	0.847	0.048	0.894	0.853	0.044	0.896
20	0.736	0.080	0.811	0.732	0.082	0.808	0.733	0.082	0.809
30	0.586	0.120	0.692	0.586	0.121	0.695	0.586	0.121	0.695
40	0.418	0.156	0.548	0.419	0.157	0.550	0.418	0.155	0.545
50	0.262	0.175	0.394	0.262	0.176	0.396	0.262	0.176	0.394
55	0.195	0.176	0.319	0.197	0.176	0.321	0.196	0.176	0.321
60	0.139	0.169	0.250	0.139	0.168	0.281	0.139	0.169	0.249
70	0.059	0.133	0.132	0.059	0.133	0.310	0.058	0.134	0.131
80	0.018	0.073	0.055	0.018	0.073	0.329	0.017	0.074	0.057
89	0.001	0.008	0.029	0.001	0.008	0.333	0.002	0.008	0.030

distribution f' coincide with those for the original distribution f throughout the whole range of θ_0 (from 0° to 90°). On the other hand, the average values of $\cos^2\theta$ for the deduced distribution f' begin to deviate from those of the original distribution f when θ_0 is greater than 55°. The average value of $\cos^2\theta$ for the original distribution f decreases continuously from 1 to 0 as θ_0 increases from 0° to 90°. However, the average value of $\cos^2\theta$ for the deduced distribution f' remains almost unchanged for $\theta_0 > 55°$, whereas it decreases continuously from 1 to 0.33 as θ_0 goes from 0° to 55°. The $\langle\cos^2\theta\rangle$ value of 0.33 at $\theta_0 = 55°$ means that an order parameter defined as

$$P_2 = \langle 3\cos^2\theta - 1\rangle/2 \tag{11}$$

is zero, representing isotropic orientation for the adsorbed molecules along the surface normal direction (z axis). For $\theta > 55°$, the conventional maximum-entropy method gives almost a constant $\langle\cos^2\theta\rangle$ of about 0.3 instead of low values, since the maximum-entropy method essentially provides the widest distribution and there is no constraint in $\langle\cos^2\theta\rangle$ in the conventional maximum-entropy method. Thus the deduced distribution determined using the conventional maximum-entropy method cannot reproduce the original distribution f. These results indicate that the six constraint functions used are insufficient to deduce correct information about the distribution. In the six constraint functions f_i, it can be seen that they are composed of the combinations of Legendre polynomials such as $P_l(\theta)$ and $P_l(\phi)$ $(l = 1-3)$ except for $P_2(\theta)$ (or $\cos^2\theta$). The missing $P_2(\theta)$ (or $\cos^2\theta$) in the constraint functions causes the lack of information about $\langle\cos^2\theta\rangle$, resulting in an erroneous distribution f' different from the original f. Therefore, we suggest that a function of $f_7 = \cos^2\theta$ must be included in the constraint functions.

Next we recalculated the distribution f'' using this modified maximum-entropy method with the seven constraint functions. The results for f'' are shown in Figs. 1(d)–1(f), from which it is clear that the deduced distributions f'' coincide with the original Gaussian distributions f irrespective of θ_0. Moreover, the respective values of the parameters $\langle\cos\theta\rangle$, $\langle\cos^3\theta\rangle$, and $\langle\cos^2\theta\rangle$ are shown to be identical for f and f'' (see Table I). Therefore, the correct distributions using this modified maximum-entropy method can be determined.

Then our modified maximum-entropy method for the case of C_{1v} symmetry was tested. A theoretical arbitrary distribution function f was used:

$$f(\theta,\phi) = C_1\exp\{-[\theta-\theta(\phi)]^2/2\sigma^2(\phi)\}[1 + d_1\cos\phi + d_2\cos2\phi + d_3\cos3\phi], \tag{12}$$

where

$$\theta(\phi) = \theta_0[1 + a_1\cos\phi + a_2\cos2\phi + a_3\cos3\phi],$$

$$\sigma(\phi) = \sigma_0[1 + b_1\cos\phi + b_2\cos2\phi + b_3\cos3\phi].$$

Note that this distribution allows both the molecular tilt angle θ and the width σ to depend on ϕ. With the arbitrary values of a_i, b_i, and d_i $(i = 1-3)$, the values of $\langle f_i\rangle$ that are responsible for SHG can be calculated. With these $\langle f_i\rangle$ values, we calculated the distribution function f' using the conventional maximum-entropy method and the distribution function f'' using the modified maximum-entropy method and compared the distribution function f with the distribution functions f' and f''. One of the comparisons is shown in Fig. 2. In this case, we used $a_1 = 0.20$, $a_2 = 0.10$, $a_3 = 0.05$, $b_1 = 0.10$, $b_2 = 0.05$, $b_3 = 0.01$, $d_1 = 0.50$, $d_2 = 0.20$, $d_3 = 0.10$, $\theta_0 = 60°$, and $\sigma_0 = 10°$. As shown in the figure, the deduced distribution f' [Fig. 2(b)] determined using the conventional maximum-entropy method is almost the same as the original distribution function f [Fig. 2(a)] except for the orientation at $\theta = 180°$. The distribution density at $\theta = 180°$ for f' is not zero, whereas that for the original f is zero. Once more it is shown that the conventional maximum-entropy method gives an erroneous orientational distribution also for the case of C_{1v}. On the other hand, when we use the modified maximum-entropy method with the constraint function of $f_7 = \cos^2\theta$, it is clear that the deduced distribution function f'' [Fig. 2(c)] is almost the same as the original distribution function f even at $\theta = 180°$.

The average values of the parameters $\langle f_i\rangle$ were also calculated. The results are summarized in Table II. When we compare the values of $\langle f_i\rangle$ $(i = 1-7)$ for the distributions f with those of f', all of the values of f are almost identical to those of f' except for the value of $\langle f_7\rangle(\langle\cos^2\theta\rangle)$. On the other hand, for the case of f'', all the $\langle f_i\rangle$ values including $\langle f_7\rangle$ for f'' are almost the same as those of f. Thus it can be concluded that the modified maximum-entropy method is also valid for the determination of orientational distribution functions for C_{1v} symmetry.

B. Examples of the orientational distribution functions of the molecular layer

Now the modified maximum-entropy method is applied to the experimental results obtained previously. Based on the experimental values of the ratios of six χ_{ijk} elements, the distribution functions were calculated using conventional and modified maximum-entropy methods and the results were compared.

For the first case, we take as an example a 4′-*n*-octyl-4-cyanobiphenyl (8CB) LC monolayer on unrubbed polyimide alignment layer, which has $C_{\infty v}$ symmetry [1]. Using the experimental results of $\chi_{zzz}:\chi_{zyy} = 1.1:3.7$, we obtained distribution a using the conventional method and distribution b using the modified method. Distributions a and b are plotted in Figs. 3(a) and 3(b), respectively. Distribution a exhibits two peaks at $\theta = 60°$ and $\theta = 180°$, while distribution b exhibits only one peak at $\theta = 77°$. The percentage of molecules at $\theta = 180°$ in distribution a is approximately 34%, while that in distribution b is zero. As shown in Sec. III A, this large distribution at $\theta = 180°$ in distribution a is an artifact. This is due to lack of the information about axial ordering ($\langle\cos^2\theta\rangle$) from the conventional maximum-entropy method. If one uses the conventional maximum-entropy method, results can be easily misinterpreted that these molecules at $\theta = 180°$ point their polar end group away from the substrate surface while the rest of the molecules points their polar group towards the surface. Another peak in distribution a also shifts towards a lower value of θ than that in distribution b. This is caused by the presence of the ghost peak at θ

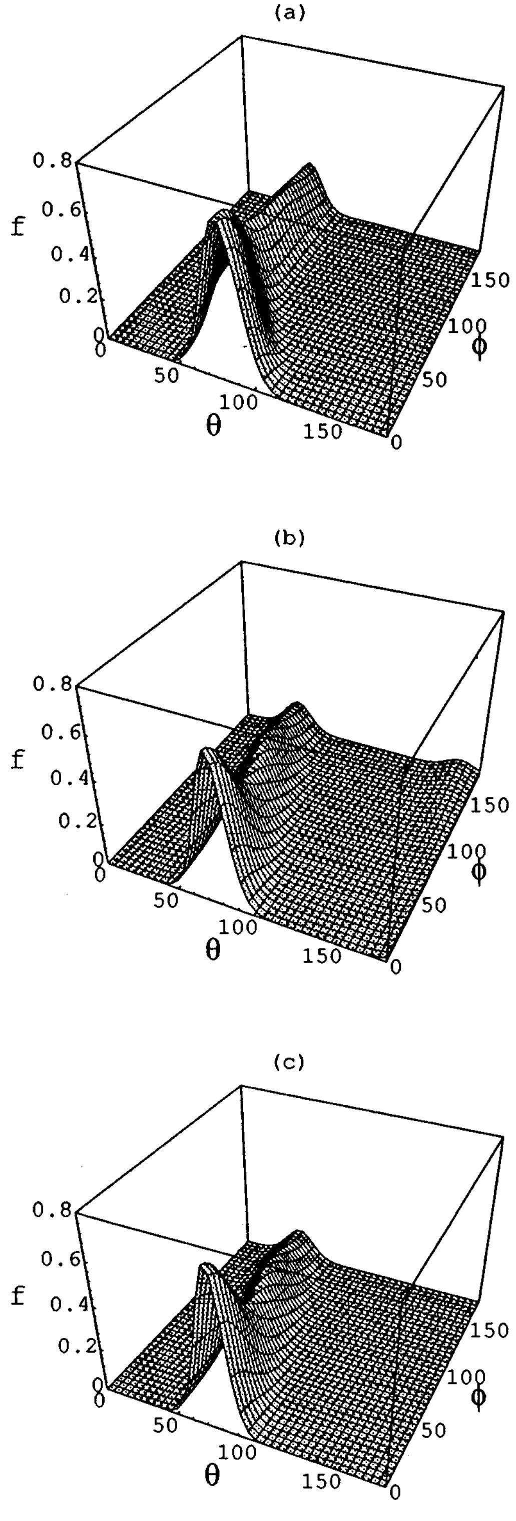

FIG. 2. Three-dimensional plots of orientational distribution functions: (a) the original distribution function f given by Eq. (12), (b) the deduced distribution f' determined using the conventional maximum-entropy method, and (c) the deduced distribution f'' determined using the modified maximum-entropy method. θ and ϕ are the tilt and azimuth angles (degree), respectively.

$=180°$ in distribution a. Applying a simplified analysis and assuming a δ-functional distribution, $\theta=69°$ is obtained. This value increases if the Gaussian distribution of a finite width is assumed. Thus the present result using the modified maximum-entropy method is also consistent with the conventional simplified analysis. Thus the P_2 $[=(3\langle\cos^2\theta\rangle-1)/2]$ value of -0.01 along the surface normal direction for distribution a is larger than that of -0.39 for distribution b. In this way, we can prove the significance of using the modified maximum-entropy method as shown by the wide difference between the two distributions.

Another example of an 8CB LC monolayer on unrubbed polyimide [2] was also tested. Using the experimental results of $\chi_{zzz}:\chi_{zyy}$ = 0.5:3.2, we obtained almost the same results as those shown in Figs. 3(a) and 3(b).

For the second case, we take as an example an 8CB LC monolayer on rubbed polyimide, which has C_{1v} symmetry [1]. Using the experimental results of $\chi_1:\chi_2:\chi_3:\chi_4:\chi_5:\chi_6$ = 0.8:1.7:1.8:3.7:0.15:0.37, we obtained distribution c using the conventional method and distribution d using the modified method. Distributions c and d are plotted in Figs. 3(c) and 3(d), respectively. Distribution c exhibits three peaks at $(\theta=57°,\ \phi=0°)$, $(\theta=64°,\ \phi=180°)$, and $\theta=180°$ with the value of $P_2=-0.09$, while distribution d exhibits only two peaks at $(\theta=72°,\ \phi=0°)$ and $(\theta=73°,\ \phi=180°)$ with $P_2=-0.37$. In this distribution c, considerable molecules are seen at $\theta=180°$, while the molecules at $\theta=180°$ do not appear in the corrected distribution d. In distribution c the other peaks also shift towards lower values of θ than those in distribution d. As shown in the figure, when the conventional maximum-entropy method is used, it is possible to overestimate the proportion of molecules oriented at $\theta=180°$. It should be noted that the distribution given by the modified method has only a small dependence of θ_{max} on ϕ. The independence between θ and ϕ has *a priori* been employed in the analysis of LC monolayers without any experimental or theoretical confirmation [4,5]. The present result using the modified maximum-entropy method provides us with proof of the independence, at least for the experiment of Ref. [1].

Another example of an 8CB LC monolayer on rubbed polyimide [2] was tested. Using the experimental results of $\chi_1:\chi_2:\chi_3:\chi_4:\chi_5:\chi_6$ = 0.4:$-$1.7:1.8:3.8:$-$0.1:$-$0.4, results almost identical to those shown in Figs. 3(c) and 3(d) were obtained. The independence of θ and ϕ was also seen in this case.

Next, for the third case, other example of 8CB molecules on rubbed polyimide [9] were tested. Taking the experimental results of $\chi_1:\chi_2:\chi_3:\chi_4:\chi_5:\chi_6$ = 1:$-$0.67:1.18:1.50:$-$0.10:$-$0.25, we obtained distribution e using the conventional method and distribution f using the modified method. Distributions e and f are plotted in Figs. 3(e) and 3(f), respectively. Distribution e exhibits three peaks at $(\theta=62°,\ \phi=0°)$, $(\theta=56°,\ \phi=180°)$, and $\theta=180°$ giving a P_2 value of -0.09, while distribution f exhibits only two peaks at $(\theta=64°,\ \phi=0°)$ and $(\theta=58°,\ \phi=180°)$ giving a P_2 value of -0.15 along the surface normal. In distribution e most molecules are seen at $\theta=180°$, while in the corrected distribution f no molecules are found at $\theta=180°$. In distribution e the other peaks also shift towards lower values of θ than those in distribution f. As shown in the figure, the proportion of molecules oriented at $\theta=180°$ can be overestimated when using the conventional maximum-entropy method. In this case, θ_{max} changes with ϕ, indicating that the simplified distribution function assuming the independence of θ and ϕ, Eq. (1), is not always valid.

TABLE II. Average values of the parameters $\langle f_i \rangle$ for the original f, the deduced f' determined by the conventional maximum-entropy method, and the deduced f'' determined by the modified maximum-entropy method.

Function	$\langle f_1 \rangle$	$\langle f_2 \rangle$	$\langle f_3 \rangle$	$\langle f_4 \rangle$	$\langle f_5 \rangle$	$\langle f_6 \rangle$	$\langle f_7 \rangle$
f	0.116	−0.291	0.135	0.136	−0.005	−0.064	0.205
f'	0.115	−0.292	0.138	0.139	−0.003	−0.065	0.231
f''	0.117	−0.292	0.139	0.140	−0.002	−0.065	0.203

Finally, we take an example of rubbed polymer with LC-substituted side chains, which give rise to SHG activity [18]. Using the experimental results of $\chi_1{:}\chi_2{:}\chi_3{:}\chi_4{:}\chi_5{:}\chi_6 = 1{:}-0.63{:}0.75{:}0.78{:}0.05{:}-0.21$, we obtained distribution g using the conventional method and distribution h using the modified method. Distributions g and h are plotted in Figs. 3(g) and 3(h), respectively. Distribution g exhibits three peaks at (θ=67°, ϕ=0°), (θ=44°, ϕ=180°), and (θ=169°, ϕ=180°) (very small) giving a P_2 value of -0.02 along the surface normal, while distribution h exhibits only two peaks at (θ=67°, ϕ=0°) and (θ=44°, ϕ=180°), giving a P_2 value of -0.04. In distribution g a small number of molecules are seen at θ=180°. In contrast, no molecules can be found at θ=180° in the corrected distribution h. The similar distributions between g and h are a consequence of the distribution at relatively small tilt angles with respect to the magic angle.

IV. CONCLUSIONS

To summarize, the determination of the orientational distribution function of organic molecular monolayers from second-order nonlinear coefficients were studied using the maximum-entropy method. It was shown that the conventional maximum-entropy method does not give sufficient information about the axial ordering along the surface normal, though the distribution function could be obtained without any bias. As a consequence, the molecular density adsorbed

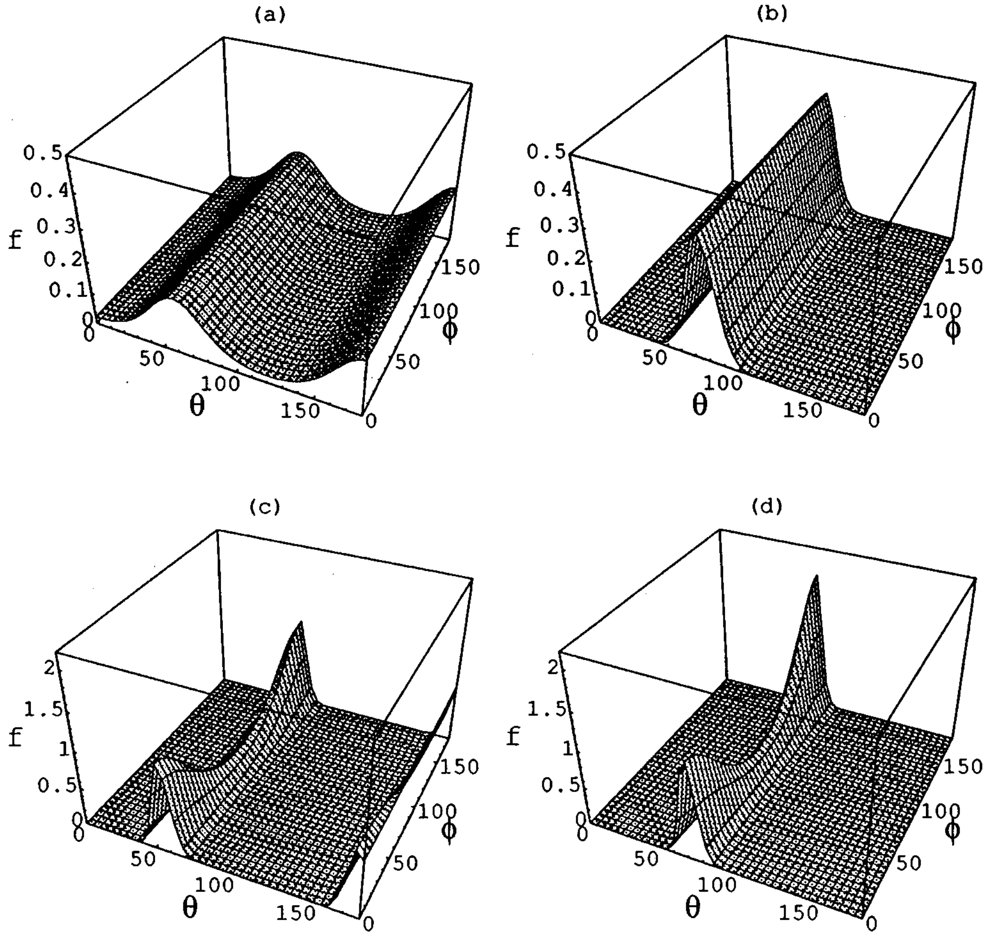

FIG. 3. Three-dimensional plots of the deduced orientational distribution functions obtained for the four experimental results reported previously. θ and ϕ are the tilt and azimuth angles (degree), respectively. The left and right columns display the results determined using the conventional and the modified maximum-entropy methods, respectively.

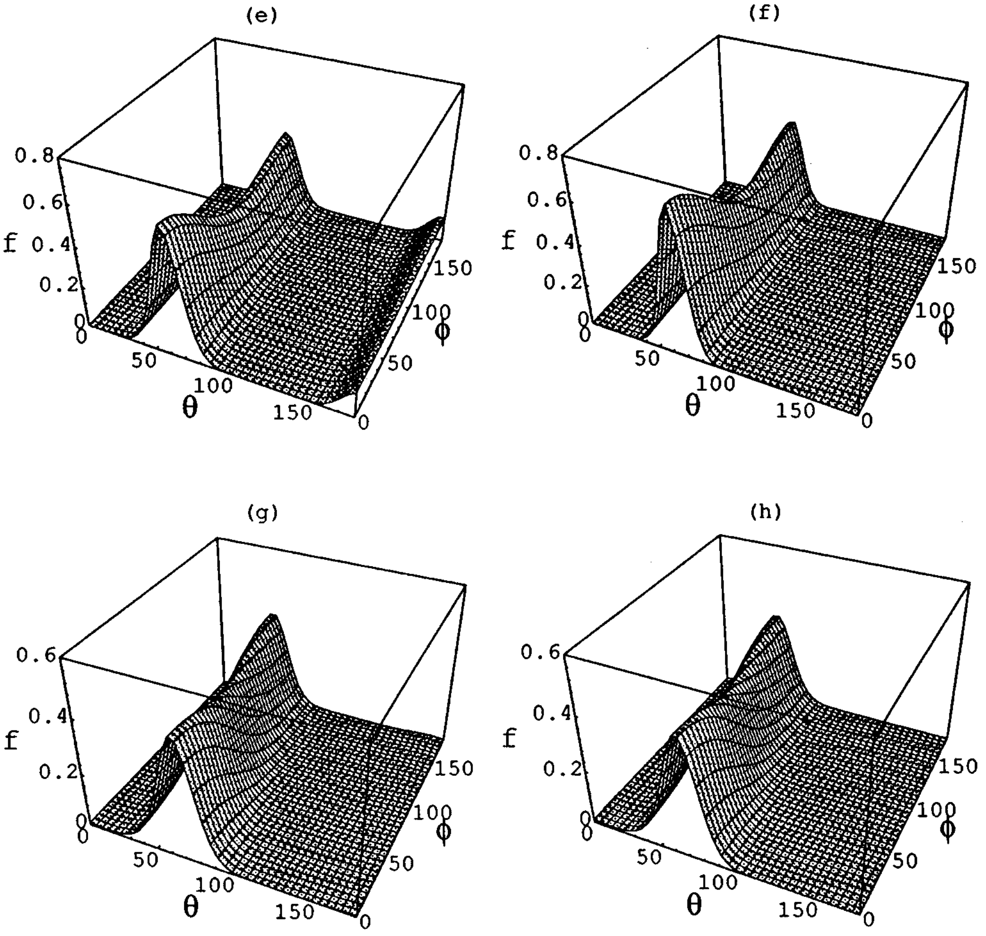

FIG. 3 (*Continued*).

at $\theta = 180°$ on the surface or at the interface may be overestimated when using the conventional maximum-entropy method. We proposed a modified method that involves the constraint function $f_7 = \langle \cos^2\theta \rangle$ as well as the six constraint functions. Using this modified maximum-entropy method, more realistic distribution functions were obtained. As practical tests, the several distribution functions were calculated by applying the modified method to a variety of SHG results reported previously. This modified method proved to be applicable to surfaces, and interfaces such as Langmuir monolayer surfaces, Langmuir-Blodgett monolayer surfaces, and interfaces of polymer films.

ACKNOWLEDGMENT

B.P. would like to acknowledge the support of Korea Science & Engineering Foundation.

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