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# Anisotropy of alkyl chains of azobenzene molecules at the air/water interface observed by sum-frequency vibrational spectroscopy

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Surface-specific sum-frequency vibrational spectroscopy has been used to study the structure of alkyl chains of azobenzene molecules at the air/water interface. The results show that the alkyl chains are well aligned before UV irradiation and protruding out of the surface with a certain distribution. Although the alkyl chains become less ordered by UV irradiation following dynamical motion due to cis-trans isomerization of the azobenzene core, the alkyl chains show anisotropy in the direction perpendicular to that of the azobenzene core by linearly polarized UV irradiation.

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Langmuir monolayers have been attracting considerable attention in terms of the fact that amphiphilic monolayers are representative of two-dimensional (2D) systems that are often used as model systems to study the functions and structures of biomembranes [1]. The intricate interplay among intermolecular forces, moderate positional and orientational ordering, and the broken symmetry at the air/water interface gives rise to a variety of patterns in the mesophase region [2]. It has been discovered, for example, that an azobenzene Langmuir monolayer is liquid like in the in-plane positional ordering, but the molecular long axis is coherently tilted away from the surface normal. A class of amphiphilic derivatives of azobenzene can form a unique Langmuir monolayer showing a 2D analog of the smectic-*C* phase [3]. Such azobenzene-based molecules have extensively been studied from fundamental and application viewpoints [4–6]. Their key feature is the cis-trans photoisomerization by electronic excitation [7,8] and much more attention has been paid to molecular alignment and its anisotropy generated in Langmuir and Langmuir-Blodgett films, polymers, and liquid crystal films due to polarized UV irradiation [9–13]. Azobenzene molecules oriented in a direction parallel to the incoming electric field prefer to be excited, whereas those along the orthogonal direction prefer not to undergo isomerization. Eventually prolonged UV irradiation to the surface of azobenzene molecules results in the preferential alignment of the molecules in the direction perpendicular to the polarization through multiple isomerization reactions. The anisotropy of the molecules can be monitored by spectroscopic techniques, such as UV/vis absorption, IR spectroscopy, and second-harmonic generation measurements [12–14]. These techniques focus on monitoring azobenzene chromophores to know how their orientation and alignment are changed before and after photoirradiation. However, if an alkyl chain is attached to the azobenzene core, a question would arise about how the alkyl chain behaves under the motion of azobenzene core.

Infrared-visible sum-frequency vibrational spectroscopy (SFVS) is an effective probe for such studies [15–17]. Being surface specific, it allows a quantitative determination of molecular orientation and alignment at various surfaces and interfaces. Applications of the techniques to Langmuir and Langmuir-Blodgett films have shown that the alkyl chains protrude out into the air [18–22]. Photoirradiation to an azobenzene-based film surface, however, is known to induce an azobenzene core alignment perpendicular to the polarization direction [12–14]. One would then have an interest in knowing how the alkyl chains orient following the motion of the azobenzene cores and how the structures of the alkyl chains are changed due to the reorientation of the azobenzene cores. To see the structures of the alkyl chains of azobenzene-based molecules, we have conducted SFVS on an azobenzene monolayer at the air/water interface. Here, we report our findings.

The experimental and the theoretical background for SFVS has been described elsewhere [23]. In our experiments, however, the main laser source is a EKSPLA Nd:YAG laser with wavelength 1.06 $\mu$m, 30 mJ pulse energy, and 25 ps pulsewidth, operating at a repetition rate of 20 Hz. The infrared generation is achieved in a $AgGaS_2$ crystal by difference frequency generation (DFG) using part of a 1.06-$\mu$m laser beam and tunable near-IR radiation from an optical parametric generator as inputs (EKSPLA). The DFG stage generates IR pulses of energy 200 $\mu$J and 25 ps, tunable from 2.5 to 10 $\mu$m with a 6 $cm^{-1}$ bandwidth. The visible and IR beams were overlapped at the sample spatially and temporally with incidence angles of 45° and 57°, respectively.

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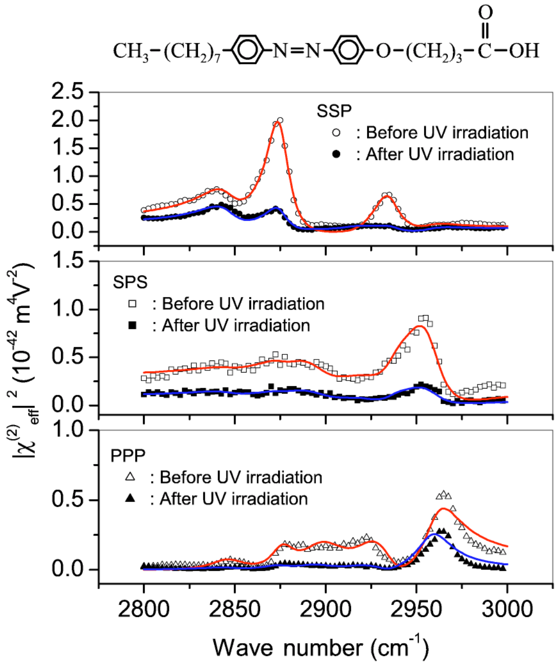

FIG. 1. SFVS spectra with SSP, SPS, and PPP, polarization combinations for a monolayer of 4-octyl-4′-(3-carboxytrimethylenoxy)azobenzene on water without and with nonpolarized UV irradiation. The nonpolarized UV at 365 nm was irradiated with ~10 mW/cm$^2$. The spectra are normalized by the SF signal from a z-cut quartz.

The sample used was a single layer of 4-octyl-4′-(3-carboxytrimethylenoxy)azobenzene, spread at the air/water interface. A stock solution was prepared by dissolving the material in chloroform and spread an appropriate amount of the solution for a full monolayer on ultrapure water (resistivity of 18.3 MΩ cm) with a precalculated area. The prepared monolayers were, more or less, in solid phase since the solution was spread into a monolayer with the excess remaining aggregated in the form of a lens so that molecules were packed as tightly as possible. This gave us relatively stable spectra. The UV irradiation of an azobenzene monolayer was made by a high-pressure mercury lamp with a band pass filter for 365 nm wavelength.

Figure 1 shows the SFVS spectra in the C-H stretch region of the azobenzene molecules at the air/water interface before and after nonpolarized UV irradiation with three input/output polarization combinations: SSP (denoting S-polarized SF output, S-polarized visible input, and P-polarized infrared input, respectively), SPS and PPP. The spectra include five C-H vibrational stretches associated with the alkyl chains and the peak assignments in the spectra are well known. The vibrational modes at approximately 2875, 2958, and 2935 cm$^{-1}$ can be assigned, respectively, to the symmetric ($r^+$) and antisymmetric ($r^-$) stretches of the terminal CH$_3$ group of the alkyl chain and the Fermi resonance ($r^+_{FR}$) between the symmetric CH$_3$ stretch and its bending mode. The modes at 2846 and 2922 cm$^{-1}$ can be assigned to the symmetric ($d^+$) and antisymmetric ($d^-$) stretches of the CH$_2$ groups on the chain, respectively. The strengths of these modes are essentially weaker compared to those of the CH$_3$ groups in the spectra before photoirradiation, indicating that the alkyl chains are not all completely trans and contain a few gauche defects. The orientation of the terminal CH$_3$ group can be determined by analyzing the $r^+$ mode [23]. This mode has a $C_{3v}$ symmetry and can only be excited if the IR polarization is along the symmetry axis. As a result, there are only two nonvanishing independent elements in the hyperpolarizability tensor, $\alpha^{(2)}_{\zeta\zeta\zeta}$ and $\alpha^{(2)}_{\xi\xi\zeta}=\alpha^{(2)}_{\eta\eta\zeta}=r\alpha^{(2)}_{\zeta\zeta\zeta}$. Here we take the symmetry axis as $\zeta$, and $\xi$ is such that one CH bond is in the $\xi\zeta$ plane as depicted in Fig. 2, and $r$ is the depolarization ratio. We can then deduce the orientational distribution of the CH$_3$ group using the same analysis described in Ref. [23]. In the case of an azimuthally isotropic interface, there are only four independent nonvanishing elements of the third-rank tensor $A_q$ for each vibrational mode: $(A_q)_{xxz}=(A_q)_{yyz}$, $(A_q)_{xzx}=(A_q)_{yzy}$, and $(A_q)_{zxx}=(A_q)_{zyy}$, $(A_q)_{zzz}$ [24]. They can be determined together with the other parameters from fitting of the SFVS spectra obtained with different input/output polarization combinations. Since each $(A_q)_{ijk}$ element is related to the molecular hyperpolarizability $\alpha^{(2)}$, we can find for an azimuthally isotropic surface the ratio of the effective $(A_q)$ values for different polarization combinations. The ratio of the effective $(A_q)$ of the $r^+$ mode between the SSP and PPP is given by

$$\frac{A^{(2)}_{r^+,\mathrm{eff}}(ppp)}{A^{(2)}_{r^+,\mathrm{eff}}(ssp)}=0.0363\frac{(\langle\cos\theta\rangle-\langle\cos^3\theta\rangle)(1-r)}{\langle\cos\theta\rangle(1+r)-\langle\cos^3\theta\rangle(1-r)}+\left(\frac{0.9781}{n'^4}\right)\frac{2(r\langle\cos\theta\rangle+\langle\cos^3\theta\rangle(1-r))}{\langle\cos\theta\rangle(1+r)-\langle\cos^3\theta\rangle(1-r)}-0.74, \tag{1}$$

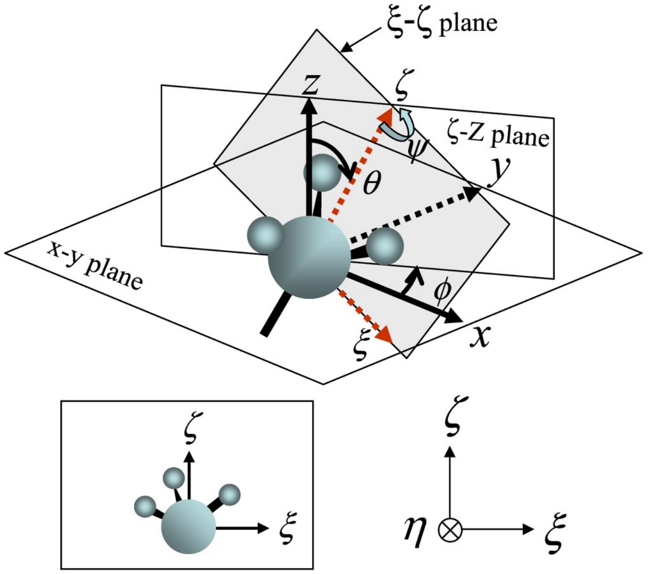

FIG. 2. Geometrical relations between the molecular and laboratory coordinates.

TABLE I. Parameters and Fresnel factors used for the calculation of $A^{(2)}_{r^+,\mathrm{eff}}$. $\epsilon'_{\mathrm{SF}} \approx \epsilon'_{\mathrm{vis}} \approx 1.32$ and $\epsilon'_{\mathrm{IR}} \approx 1.28$ calculated as in Ref. [23].

| | $\omega_{\mathrm{SF}}$ | $\omega_{\mathrm{vis}}$ | $\omega_{\mathrm{IR}}$ |
|---|---|---|---|
| Wavelength λ ($\mu$m) | 0.810 | 1.064 | 3.47 |
| Refractive index $n$ (water) | 1.328 | 1.324 | 1.284 |
| Beam angle $\beta$ (deg) | 47.8 | 45.0 | 57.0 |
| Fresnel factor $L_{xx}$ | 0.964 | 0.951 | 1.040 |
| Fresnel factor $L_{yy}$ | 0.757 | 0.773 | 0.718 |
| Fresnel factor $L_{zz}$ | $1.036/\epsilon'_{\mathrm{SF}}$ | $1.049/\epsilon'_{\mathrm{vis}}$ | $0.960/\epsilon'_{\mathrm{IR}}$ |

where we used $r = 2.2$, which is a theoretically obtained value [25,26], and the Fresnel factors and geometrical parameters needed for calculation are listed in Table I; here, $n'$ was determined with a simple estimate of the local-field correction at the interface using the modified Lorentz model [23]. We can then deduce the polar angle $\theta_0$ of the $CH_3$ group with its distribution $\sigma$ assuming a Gaussian distribution function. Figure 3 plots the relationship of $A^{(2)}_{r^+,\mathrm{eff}}(ppp)/A^{(2)}_{r^+,\mathrm{eff}}(ssp)$ to the possible polar tilt angle $\theta_0$ of the $CH_3$ group with the distribution $\sigma$. From the experimentally determined ratio $A^{(2)}_{r^+,\mathrm{eff}}(ppp)/A^{(2)}_{r^+,\mathrm{eff}}(ssp) \approx -0.25$, we deduce $\theta_0 \approx 46°$ with the $\delta$ function, $\theta_0 \approx 48°$ with $\sigma = 10°$, $\theta_0 \approx 52°$ with $\sigma = 20°$, and $\theta_0 \approx 60°$ with $\sigma = 30°$.

As seen in Fig. 1, the photoirradiation did reduce the intensity of the whole spectra and the ratio of the $d^+$ mode with the $r^+$ mode became larger, indicating that the alkyl chains in a monolayer of azobenzene molecules are more randomly distributed and highly disordered. This is presumably because the cis-trans multiple isomerization causes rapid motion of azobenzene chromophores and the chain-chain interaction would be weakened during the reaction. As a result, the chains must be highly disordered with a large number of defects so that both $CH_2$ and $CH_3$ groups can randomly be oriented in the monolayer, yielding a vanishingly small SF signal due to near inversion symmetry [27]. The final spectra in which only a small SF signal appears were approximately the same irrespective of the power of irradiation, although the time to reach the steady state is different. The spectra obtained with UV irradiation were not recovered to the initial spectra when the irradiation was terminated, suggesting that the structural changes of alkyl chains at the air/water interface are irreversible. The disordered alkyl chains may eventually lie down to the surface of water and would not be able to stick out into the air any more. We have found, however, that the alkyl chains behave differently when we used the linearly polarized light between the relatively strong and weak power irradiation.

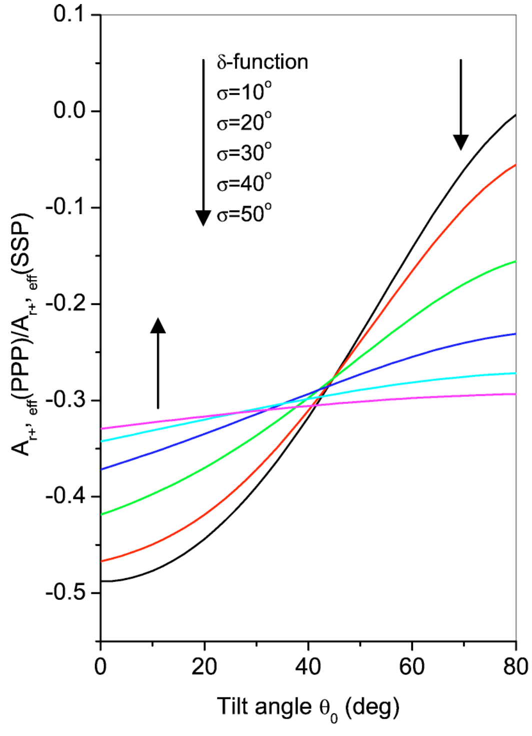

FIG. 3. Relationship between $A^{(2)}_{r^+,\mathrm{eff}}(ppp)/A^{(2)}_{r^+,\mathrm{eff}}(ssp)$ and the polar tilt angle $\theta_0$ of the $CH_3$ group.

Shown in Fig. 4 are the spectra that are obtained by linearly polarized UV irradiation. In the case of weak power irradiation, clear anisotropy can hardly be seen as in Fig. 4(a). However, the distinct anisotropy of the alkyl chains could be observed under the relatively strong excitation with the linearly polarized light as seen in Fig. 4(b). From the obtained spectra that exhibit the anisotropy, the alkyl chain orients preferentially along the polarization axis rather than the direction perpendicular to the polarization axis. It is well known that the azobenzene cores prefer to be aligned along the direction perpendicular to the polarization through multiple cis-trans isomerization [9–13]. This allows us to understand that liquid crystal molecules adsorbed on a polarized UV irradiated azobenzene film preferentially align along the direction perpendicular to the polarization axis [13,14]. Interestingly, the anisotropy of the alkyl chains that we observed is a 90° different direction compared to that of the azobenzene cores. We have done several confirmations to prove the appearance of the anisotropy of the alkyl chains. Even changing the order of the measurements for polarization directions also provided the appearance of anisotropy. Furthermore, we did change the polarization direction or the power of UV irradiation while monitoring the SF signal generated from the $CH_3$ stretch. Figure 5 shows the time-dependent $r^+$ SF signal with the wave number fixed at 2875 $\mathrm{cm}^{-1}$. The SF signal was significantly increased when the polarization direction was changed from perpendicular to parallel to the incident plane. We also observed a significant increase of the SF signal as the power of irradiation was increased with the polarization parallel to the incident plane. These can be regarded as evidence of the result that the alkyl chains are controlled by polarized light and the anisotropy of the chain appears under linearly polarized UV irradiation.

The photoexcitation let the absolute ratio between the SSP and PPP amplitudes of the $r^+$ mode become smaller and close to zero by the linearly polarized UV irradiation, since the $r^+$ mode becomes discernible in the PPP spectrum like

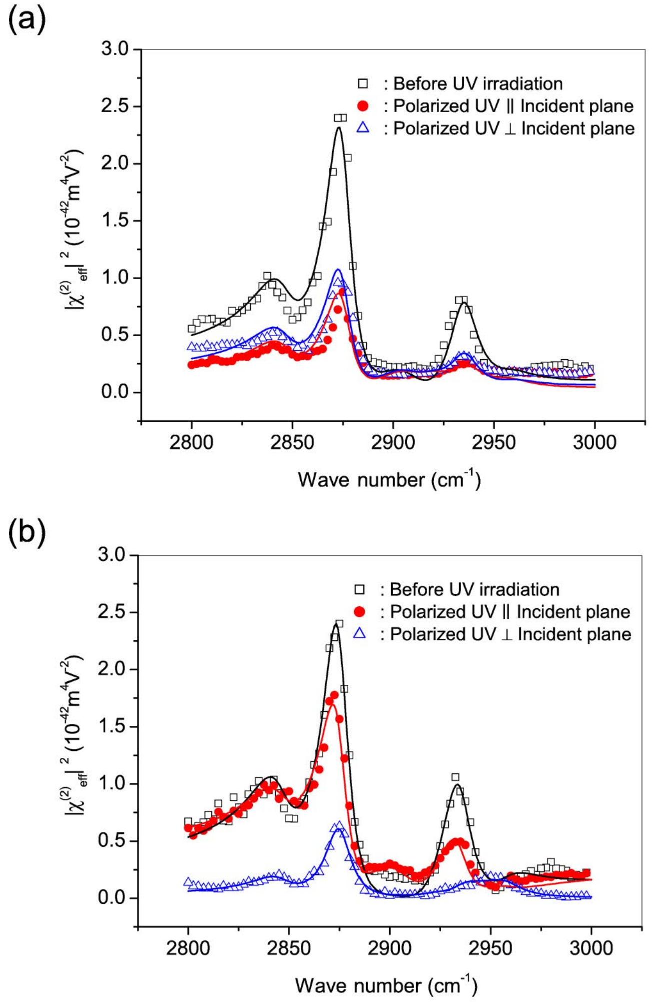

FIG. 4. SFVS spectra of a monolayer of 4-octyl-4′-(3-carboxytrimethylnoxy)azobenzene on water with linearly polarized UV irradiation. The linearly polarized UV was irradiated (a) with ~0.2 mW/cm$^2$ and (b) with ~10 mW/cm$^2$.

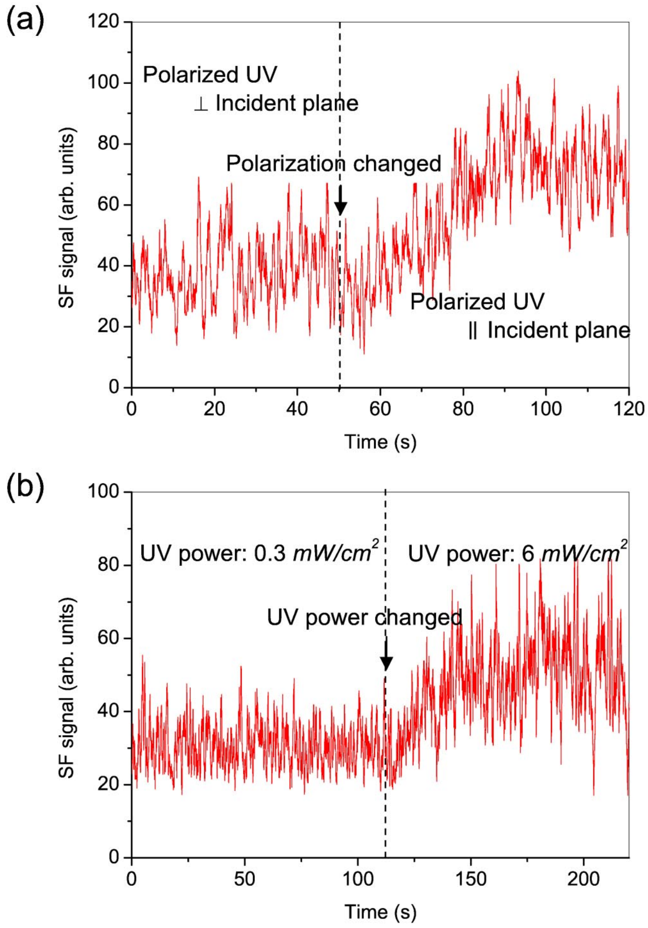

FIG. 5. Time-dependent SF signal of the $r^+$ mode (a) before and after the polarization direction of UV was changed and (b) before and after the power of UV irradiation was increased.

the bottom spectrum in Fig. 1. The $d^+$ mode remained constant while the peak related to the $r^+$ mode decreased in Fig. 4. These facts indicate that the alkyl chains become disordered under UV irradiation irrespective of nonpolarized and polarized light. It would also be an undeniable possibility that the surface pressure area of azobenzene is largely increased, and a disordered monolayer is formed on the top of the first monolayer. This may result in the weak signal observed in Fig. 4(a) despite the weak UV irradiation. However, we did confirm the distinct in-plane anisotropy by the time evolution of the signal that goes from a small to a large signal associated with the change of the polarization direction. A larger signal in a given direction corresponds to larger ordering along the same direction. The anisotropy could be observed above a certain fluence, around ~1 mW/cm$^2$, however, we were unable to clarify how the degree of anisotropy is different as a function of fluence. One reason is that the state at which the anisotropy was observed was not necessarily a sort of steady state presumably because of unstable molecular assembled structures, alkyl chain structures, or transition to multilayers at the air/water interface. The prolonged irradiation eventually gave us very weak signals as observed in Fig. 1 in the case of nonpolarized irradiation.

To have a more quantitative picture of the orientation of the CH$_3$ group by UV irradiation, we analyzed the ratio between the $r^+$ and $r^-$ modes using only the SSP spectra since the $r^+$ mode is discernible in the PPP spectra. Unfortunately, what we can get from the spectra is less information to deduce the orientations than in the isotropic case although more information is required due to the lower symmetry at the surface by UV irradiation. So assuming here the free rotation $\psi$ of the CH$_3$ group about the symmetric axis, we take account of only the azimuthal $\phi$ and the tilt $\theta$ angles from the surface normal. Since the mode amplitude $A^{(2)}_{q,\mathrm{eff}}(\gamma,ssp)$ is written by $A^{(2)}_{q,\mathrm{eff}}(\gamma,ssp) \propto (A^{(2)}_q)_{yyz}\cos^2\gamma + (A^{(2)}_q)_{xxz}\sin^2\gamma$, we can deduce the amplitudes for the $r^+$ and $r^-$ modes from the SSP spectra which exhibit anisotropy, $(A^{(2)}_{r^+})_{xxz}$, $(A^{(2)}_{r^-})_{xxz}$, $(A^{(2)}_{r^+})_{yyz}$, $(A^{(2)}_{r^-})_{yyz}$. The polarization direction of UV irradiation is geometrically along the $x$ axis ($\gamma=0°$) or along the $y$ axis ($\gamma=90°$). The ratios $(A^{(2)}_{r^-})_{yyz}/(A^{(2)}_{r^+})_{yyz}$ and $(A^{(2)}_{r^-})_{xxz}/(A^{(2)}_{r^+})_{xxz}$ are given by

$$\left|\frac{(A^{(2)}_{r^-})_{yyz}}{(A^{(2)}_{r^+})_{yyz}}\right| = \left| -2\frac{\alpha^{(2)}_{\zeta\eta\eta}}{\alpha^{(2)}_{\zeta\zeta\zeta}} \frac{(\cos\theta-\cos^3\theta)\sin^2\phi}{[\cos\theta(r\cos^2\phi+\sin^2\phi)-\cos^3\theta\sin^2\phi(1-r)]}\right|, \tag{2}$$

$$\left|\frac{(A^{(2)}_{r^-})_{xxz}}{(A^{(2)}_{r^+})_{xxz}}\right| = \left| -2\frac{\alpha^{(2)}_{\zeta\eta\eta}}{\alpha^{(2)}_{\zeta\zeta\zeta}} \frac{(\cos\theta-\cos^3\theta)\cos^2\phi}{[\cos\theta(r\sin^2\phi+\cos^2\phi)-\cos^3\theta\cos^2\phi(1-r)]}\right|, \tag{3}$$

where $\alpha^{(2)}_{\zeta\eta\eta}/\alpha^{(2)}_{\zeta\zeta\zeta}=4(1-R)/(1+8R)\approx 1.62$. Here $R$ is the depolarization ratio of a CH single bond and we use $R\approx 0.14$ [25,26], and we simply assume $\delta$ functions for both $\theta$ and $\phi$. Figures 6(a) and 6(b), respectively, show contour plots for the calculated $|(A^{(2)}_{r^-})_{yyz}/(A^{(2)}_{r^+})_{yyz}|$ and $|(A^{(2)}_{r^-})_{xxz}/(A^{(2)}_{r^+})_{xxz}|$ values as functions of $\theta$ and $\phi$. From the experimentally determined values $|(A^{(2)}_{r^-})_{yyz}/(A^{(2)}_{r^+})_{yyz}|=0.13$ and $|(A^{(2)}_{r^-})_{xxz}/(A^{(2)}_{r^+})_{xxz}|=0.91$, we can deduce the values of $\theta\approx 47°$ and $\phi\approx 22°$ from Fig. 6. These values give us a picture that the $CH_3$ group indeed orients along the linearly polarized UV direction.

The anisotropy of the alkyl chains is a resultant state from the dynamics of the isomerization of the azobenzene core. Since each molecule stands on water unstably and can migrate during the isomerization process, the alkyl chains may prefer to intrude into the neighboring space where another molecule sat just a moment ago. This could be the reason why the alkyl chains become less ordered under UV irradiation. That the axis of the alkyl chain is along the orthogonal direction to the axis of the azobenzene core under UV irradiation would be a reasonable observation if we consider a bent-shaped molecule of the cis-isomer of the azobenzene core. The $C_2$ symmetry of linearly polarized UV irradiation allows each principal axis to be either parallel or perpendicular to the linear polarization axis. If the axis of the alkyl chain is tilted away from that of the azobenzene core, the remaining component of the axis of the alkyl chain can be parallel to the polarization axis and along the orthogonal direction to the azobenzene core, as the statistical average, which preferentially aligns along the direction perpendicular to the polarization. This is because there is ambiguity of either the parallel or antiparallel direction about the direction of the axis of azobenzene core. Assuming that the azobenzene core is fixed and the axis of the alkyl chain is freely rotated around the axis of the core, the magic angle can be the critical angle to determine the axis of the alkyl chain. It is parallel to the azobenzene core if the angle with respect to the axis of the azobenzene core is smaller than the magic angle. A larger angle than the magic angle, however, allows the axis of the alkyl chain to be along the orthogonal direction to the azobenzene core. Presumably this would be the case for the cis-isomer azobenzene molecule with an alkyl chain, although it would not be so clear how the axis of the cis-isomer azobenzene core is determined. Knowing the results and arguments, our observations about the alkyl chain would reflect and be consistent with the isomerization of the azobenzene core.

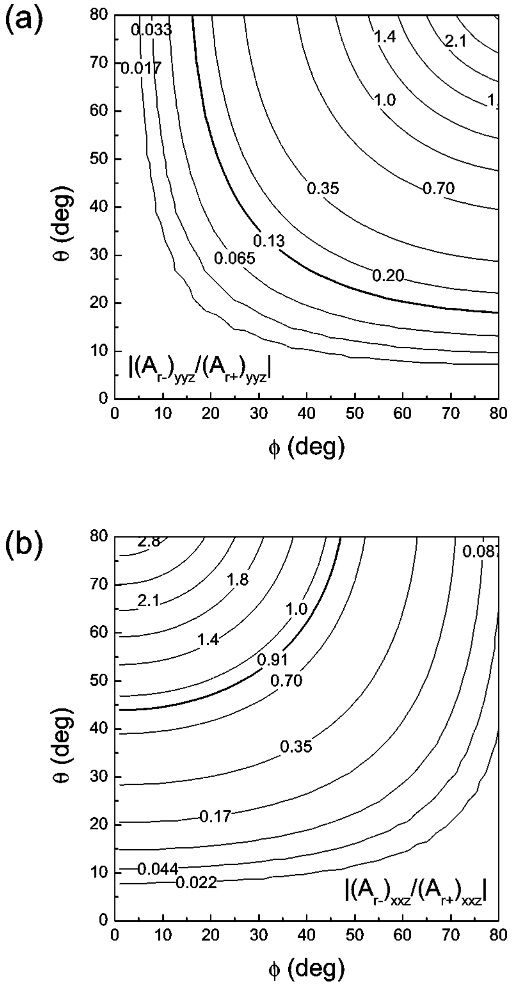

FIG. 6. (a) Contour lines for $|(A^{(2)}_{r^-})_{yyz}/(A^{(2)}_{r^+})_{yyz}|$ and (b) $|(A^{(2)}_{r^-})_{xxz}/(A^{(2)}_{r^+})_{xxz}|$ as functions of $\theta$ and $\phi$ of the $CH_3$ group.

In conclusion, we have shown that the alkyl chains are well ordered in a monolayer of azobenzene molecules before UV irradiation. We have also observed a strong disordering of alkyl chains by nonpolarized UV irradiation. Although linearly polarized UV irradiation forces the alkyl chains to be less ordered due to the motion of isomerization of the azobenzene cores, anisotropy of the alkyl chains can be observed under linearly polarized UV irradiation. The direction of the anisotropy is the 90° difference from the well-known anisotropy of azobenzene cores which is perpendicular to the polarization axis.

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