

Sum-Frequency Vibrational Spectroscopic Study of a Rubbed Polymer Surface

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Sum-frequency vibrational spectroscopy has been used to probe the chain orientation of polyvinyl alcohol at the surface after rubbing. The distribution function of the chain orientation is determined quantitatively. The orientational order parameter of the chains deduced from the distribution matches well with that of a liquid crystal monolayer deposited on the polymer, proving that the polymer surface can align a liquid crystal film through orientational epitaxy. [S0031-9007(99)09202-9]

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Among modern strategic materials, polymers have become increasingly important in our daily life. In many applications, polymer interfaces play a pivotal role. Often it is the orientation and conformation of molecular units at a polymer surface that determine the polymer interfacial properties. For example, surface molecular orientation directly affects adhesion of a polymer to metals or semiconductors, which is vital to modern electronic devices and systems [1]. Surface molecular conformation of a biopolymer, such as protein, DNA, and RNA, strongly influences binding of ligands to a substrate and hence the enzymatic function of the biopolymer [2]. A polymer surface with oriented polymer chains could serve as a template for growing highly ordered polymeric or organic crystals superb in mechanical, electrical, thermal, or optical properties [3]. As a more specific case, rubbed polymer films have long been used in the liquid crystal display industry as substrates for obtaining the desired liquid crystal (LC) bulk alignment. Rubbing presumably modifies the polymer surface structure, and then aligns the LC [4,5]. To study how rubbing affects the polymer surface structure, a number of techniques have been used with varying degrees of success. Ellipsometry [6] and infrared spectroscopy [7] can measure rubbing-induced anisotropy in the surface region of a polymer film, but are incapable of probing the real surface because of their lack of surface specificity. Atomic force microscopy [8] can provide images of rubbed polymer surfaces although the spatial resolution may be limited. Near-edge x-ray absorption fine structure spectroscopy [9] can probe a surface layer of 1 nm thick and yield information on the orientational order parameter of a rubbed polymer surface.

Recently, sum-frequency generation (SFG) vibrational spectroscopy has been demonstrated to be an effective surface analytical probe [10]. As a second-order nonlinear optical process, it is forbidden in media with inversion symmetry, but allowed at interfaces where the inversion symmetry is necessarily broken. Therefore it is particularly sensitive to the interfacial structure between two centrosymmetric media. When used to probe surface molecular orientation, it can provide information not only on the average molecular orientation and order parameter

but also on the orientational distribution. We report here application of this technique to the study of surface alignment of polymer chains by rubbing. We take polyvinyl alcohol (PVA, $[-\text{CH}_2-\text{CHOH}-]_n$, structure shown in Fig. 1) as an example. It was found that the PVA chains at the surface are indeed well aligned by rubbing. A quantitative analysis of the SFG results yielded an orientational distribution for the chains that exhibits narrow angular spreads in all three directions. To our knowledge, this is the first time that an orientational distribution of polymer chains at a surface has ever been measured. From the distribution function, the orientational order parameter was deduced. It agreed well with the measured order parameter of an LC monolayer adsorbed on the rubbed PVA, proving that orientational epitaxy is the underlying mechanism for LC alignment by rubbed PVA surfaces.

Surface SFG results from a nonlinear polarization induced at an interface by two input fields $\mathbf{E}(\omega_1)$ and $\mathbf{E}(\omega_2)$ at frequencies ω_1 (visible) and ω_2 (infrared), respectively,

$$\mathbf{P}^{(2)}(\omega_s) = \chi^{(2)} : \mathbf{E}(\omega_1)\mathbf{E}(\omega_2), \quad (1)$$

where $\chi^{(2)}$ denotes the surface nonlinear susceptibility tensor. It can be shown [10] that the SFG output intensity

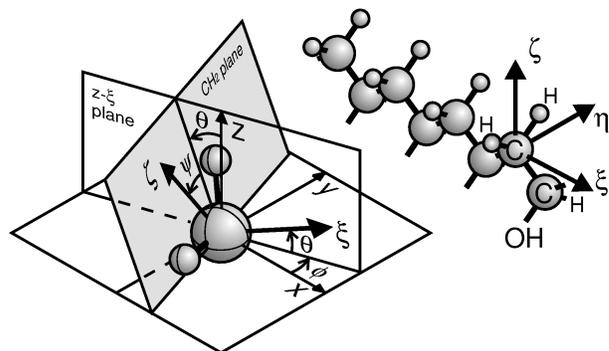


FIG. 1. Molecular structure of PVA and orientational geometry of a CH_2 group on a rubbed PVA surface. Axis x is along the rubbing direction, and z is along the surface normal of the polymer film. Axis ξ is normal to CH_2 plane (along the PVA chain), ζ is along the symmetry axis of CH_2 , and η is orthogonal to ξ and ζ .

in the reflected direction (in mks units) is given by

$$I(\omega_s) = \frac{\omega_s^2}{8\epsilon_0^3 c^3 \cos^2 \beta} |\chi_{\text{eff}}^{(2)}|^2 I(\omega_1) I(\omega_2). \quad (2)$$

Here, β is the angle of the SF output, $I(\omega_i)$ is the beam intensity at ω_i , and $\chi_{\text{eff}}^{(2)}$ is the effective surface nonlinear susceptibility defined as

$$\chi_{\text{eff}}^{(2)} = [\mathbf{e}_s \cdot \mathbf{L}(\omega_s)] \chi^{(2)} : [\mathbf{e}_1 \cdot \mathbf{L}(\omega_1)] [\mathbf{e}_2 \cdot \mathbf{L}(\omega_2)] \quad (3)$$

with \mathbf{e}_i being a unit polarization vector of the optical field at ω_i and $\mathbf{L}(\omega_i)$ the tensorial Fresnel factor. As a response function, $\chi^{(2)}$ is expected to be resonantly enhanced when ω_2 approaches a surface resonance. Scanning over resonances then yields a surface SFG spectrum. In this paper, we focus on surface vibrational spectroscopy. We can write

$$\chi^{(2)} = \chi_{NR}^{(2)} + \sum_q \frac{\mathbf{A}_q}{\omega_2 - \omega_q + i\Gamma_q}, \quad (4)$$

$$\mathbf{A}_q = N_s \langle \mathbf{a}_q \rangle_f = N_s \int \mathbf{a}_q f(\Omega) d\Omega, \quad (5)$$

where $\chi_{NR}^{(2)}$ describes the nonresonant contribution, \mathbf{A}_q , ω_q , and Γ_q are the strength, resonant frequency, and damping constant of the q th resonance mode, respectively, N_s is the surface density of molecules, \mathbf{a}_q is the nonlinear molecular polarizability strength associated with the q th resonance, Ω denotes the set of three orientational angles (θ, ϕ, ψ) defined in Fig. 1, and $\langle \rangle_f$ denotes an average with the orientational distribution function $f(\Omega)$.

The experimental setup for SFG has been described elsewhere [10]. In this experiment, a visible beam at 532 nm and an IR beam tunable from 2.6 to 3.7 μm , both having a 15 ps pulse width and a 20 Hz repetition rate, were overlapped at the sample with incidence angles 45° and 57° , respectively. The SFG output was detected in the reflected direction. The rubbed PVA films were prepared by spin coating on fused quartz plates, followed by baking and rubbing with velvet. The rubbing strength used was at a saturation level; i.e., stronger rubbing would not improve the chain alignment further. The film thickness was about 30 nm.

We have measured the SFG spectra in the CH and OH stretch frequency range. The OH stretch modes are rather weak and can be identified as OH groups hydrogen bonded to their neighbors [11]. This suggests that the OH groups at the surface are oriented toward the polymer bulk. Correspondingly the CH_2 groups should point out of the surface, as evidenced by the strong CH_2 stretch modes in the spectra shown in Fig. 2. The SFG signal disappeared when the surface was immersed in water, but reappeared when it was dried. The result indicates that the spectrum must come mainly from the surface of the polymer because otherwise the spectrum would not have changed so dramatically upon a simple perturbation of the surface.

The SFG spectra of PVA were taken with different input/output polarization combinations and different

sample orientations specified by the azimuthal angle γ between the incidence plane and the rubbing direction \hat{x} . The spectra at $\gamma = 0^\circ$ and 90° are presented in Fig. 2 as examples. Only those with polarization combinations *SSP* (for *S*-, *S*-, and *P*-polarized SF output, visible input, and IR input, respectively), *SPS*, and *PPP* are shown since the others (*SSS*, *SPP*, and *PPS*) are hardly distinguishable from noise. All the measured spectra can be fit by Eq. (4) assuming the presence of three resonant modes at 2882, 2907, and 2940 cm^{-1} , each with a damping constant $\Gamma \approx 16 \text{ cm}^{-1}$. The first one, which is rather weak, probably comes from the stretch mode of the CH groups on PVA. The last two, highly prominent except for some polarization combinations, can be identified with the symmetric (*s*) and antisymmetric (*a*) stretch modes of CH_2 . Fitting of the spectra allows us to deduce the effective mode strength

$$A_{q,\text{eff}} = [\mathbf{e}_s \cdot \mathbf{L}(\omega_s)] \mathbf{A}_q : [\mathbf{e}_1 \cdot \mathbf{L}(\omega_1)] [\mathbf{e}_2 \cdot \mathbf{L}(\omega_2)] \quad (6)$$

for every specific γ and polarization combination. The deduced values are plotted in Fig. 3. In the following, we shall use them to deduce the orientation of CH_2 (and hence the orientation of PVA chains since the chains are perpendicular to the CH_2 planes) at the surface of PVA.

Without any calculation, we can already obtain definitive information from the spectra in Fig. 2. First, the

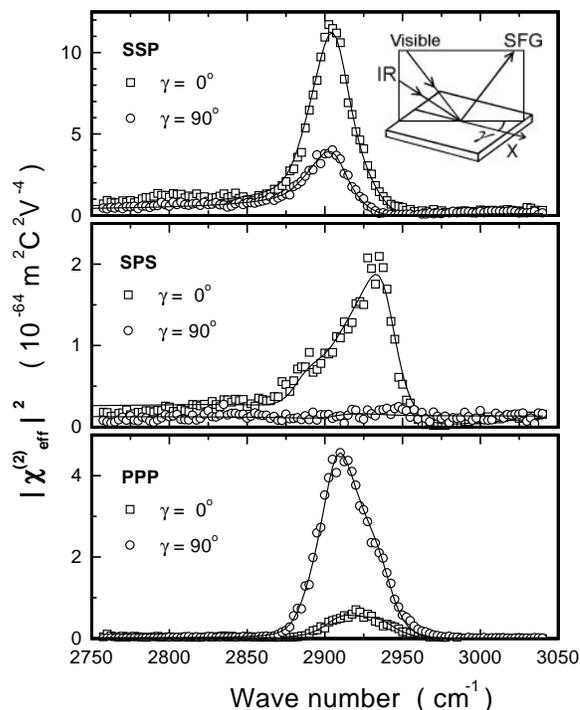


FIG. 2. SFG spectra of a rubbed PVA surface in the CH stretch range for three different polarization combinations, *SSP*, *SPS*, and *PPP*. The intensity has been calibrated with a reference *z*-cut quartz crystal. Only spectra at $\gamma = 0^\circ$ and 90° are shown. Solid lines in the figures are fits from Eq. (4). The inset defines γ for the azimuthal sample orientation.

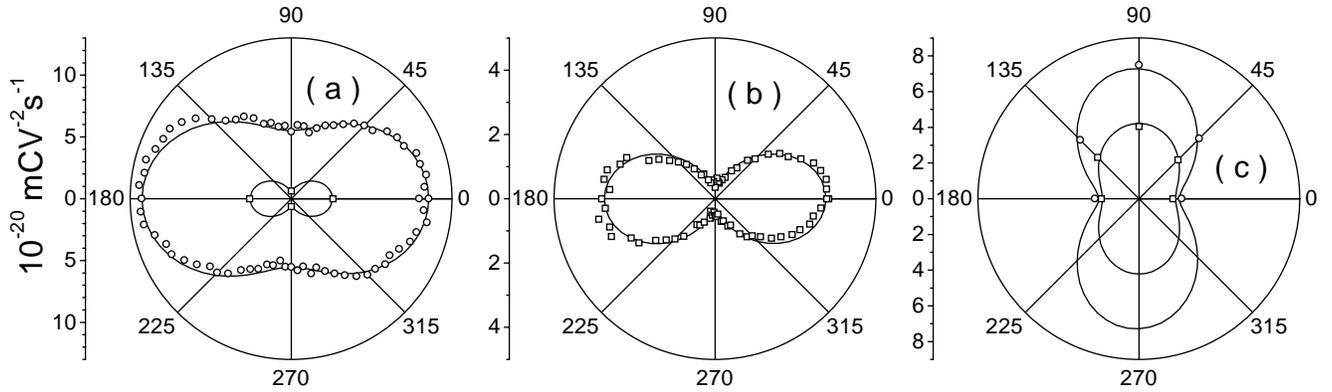


FIG. 3. Polar plots of the effective mode strength $A_{q,\text{eff}}$ of the CH_2 symmetric (circles) and antisymmetric (squares) stretch modes as functions of γ for different polarization combinations (a) *SSP*, (b) *SPS*, and (c) *PPP*. Symbols are values deduced from the measured SFG spectra. Lines are obtained from fits (see text).

excitation of the CH_2 symmetric stretch requires an IR polarization component along the symmetry axis of CH_2 . The fact that the mode is very weak in the *SPS* spectra (for all γ) indicates that the CH_2 axis must be nearly perpendicular to the surface plane. Second, the excitation of the CH_2 antisymmetric stretch requires an IR component in the CH_2 plane perpendicular to the CH_2 symmetry axis. Since this mode is absent at $\gamma = 90^\circ$ and very strong at $\gamma = 0^\circ$, the CH_2 plane must be nearly perpendicular to the rubbing direction. Consequently, the PVA chains must be oriented nearly parallel to the surface along the rubbing direction. Finally, in Fig. 3, the polar plot of $A_{s,\text{eff}}(\text{SSP})$ shows a slight forward/backward asymmetry. This indicates that the average orientation of the chains has a slight backward tilt.

We now discuss the quantitative analysis of the data. The rubbed PVA surface has C_{1v} symmetry. Therefore its nonlinear susceptibility $\chi_{ijk}^{(2)}$ [correspondingly, $(A_q)_{ijk}$ for each CH_2 mode] has only 10 nonvanishing independent elements: $xxz, yyz, zzz, xzx = zxx, yzy = zyy, xxx, yyy, zzx, xyy = yxy$, and $xzz = zxz$. There exist additional equations relating some of the $(A_q)_{ijk}$ that are specific to the CH_2 stretch vibrations. By symmetry the only nonvanishing elements of the \mathbf{a}_q tensor in Eq. (5) are $(a_s)_{\xi\xi\xi}, (a_s)_{\eta\eta\xi}, (a_s)_{\zeta\zeta\xi}$, and $(a_a)_{\eta\xi\eta} = (a_a)_{\xi\eta\eta}$, where (ξ, η, ζ) are the molecular coordinates defined in Fig. 1. It can be shown from Eq. (5) that

$$\begin{aligned} (A_s)_{xzx} + (A_s)_{yzy} + (A_s)_{zzz} &= N_s \langle \hat{\xi} \cdot \hat{z} \rangle_f (a_s)_{\xi\xi\xi}, \\ (A_s)_{xxz} + (A_s)_{yyz} + (A_s)_{zzz} &= N_s \langle \hat{\xi} \cdot \hat{z} \rangle_f \\ &\quad \times [(a_s)_{\xi\xi\xi} + (a_s)_{\eta\eta\xi} \\ &\quad + (a_s)_{\zeta\zeta\xi}], \end{aligned} \quad (7)$$

$$\begin{aligned} (A_a)_{xzx} + (A_a)_{yzy} + (A_a)_{zzz} &= N_s \langle \hat{\xi} \cdot \hat{z} \rangle_f (a_a)_{\eta\xi\eta}, \\ (A_a)_{xxz} + (A_a)_{yyz} + (A_a)_{zzz} &= 0. \end{aligned}$$

If we adopt the bond additivity model for CH_2 vibrations [12], we can find $(a_s)_{\xi\xi\xi} = 0.16a_0$, $(a_s)_{\eta\eta\xi} = 0.82a_0$, $(a_s)_{\zeta\zeta\xi} = 0.49a_0$, and $(a_a)_{\eta\xi\eta} = (a_a)_{\xi\eta\eta} = 0.66a_0$ with

$a_0 = -\frac{1}{2\omega_q} \mu' \alpha'_{\parallel} \approx 4.5 \times 10^{-38} \text{ m}^3 \text{ C V}^{-2} \text{ sec}^{-1}$, where μ' and α'_{\parallel} are the dipole derivative [13] and polarizability derivative [14] of a single CH bond. We then have, from Eqs. (7), three equations of constraints for the nonvanishing $(A_q)_{ijk}$. Taking the nonvanishing $(A_q)_{ijk}$ and the dielectric constants $\epsilon'(\omega_s) = \epsilon'(\omega_1)$ and $\epsilon'(\omega_2)$ for the surface layer [appearing in the Fresnel factors $\mathbf{L}(\omega_i)$ [10]] as unknown parameters, we can now use these equations and Eq. (6) to fit the experimental data in Fig. 3. As shown in Fig. 3, the fit is very satisfactory, yielding values of $(A_q)_{ijk}$ listed in Table I, and $\epsilon'(\omega_1) = 2.1$ and $\epsilon'(\omega_2) = 1.5$.

Knowing $(A_q)_{ijk}$, we can then use Eq. (5) to obtain an approximate orientational distribution function $f(\Omega)$ for the CH_2 groups. Knowing that the PVA chains are well aligned, we can assume a Gaussian distribution for $f(\Omega)$

$$f(\Omega) = C \exp \left[-\frac{(\theta - \theta_0)^2}{2\sigma_\theta^2} - \frac{(\phi - \phi_0)^2}{2\sigma_\phi^2} - \frac{(\psi - \psi_0)^2}{2\sigma_\psi^2} \right], \quad (8)$$

where C is a normalization constant, $\phi_0 = \psi_0 = 0^\circ$ (by symmetry), and $\theta_0, \sigma_\theta, \sigma_\phi$, and σ_ψ are the parameters

TABLE I. Measured and calculated nonvanishing tensor elements A_{ijk} for the CH_2 symmetric (*s*) and antisymmetric (*a*) stretch modes. All values are in units of $10^{-21} \text{ m C V}^{-2} \text{ sec}^{-1}$.

	<i>s</i> -stretch		<i>a</i> -stretch	
	Measured	Calculated	Measured	Calculated
A_{xxx}	200 ± 10	199	-25 ± 15	-10
A_{yyz}	420 ± 10	419	-120 ± 15	-129
A_{zzz}	310 ± 40	317	200 ± 60	140
$A_{xzx} = A_{zxx}$	~ 0	21	20 ± 20	46
$A_{yzy} = A_{zyy}$	~ 0	-27	205 ± 15	211
A_{xxx}	~ 0	-8	~ 0	-4
A_{yyx}	-17 ± 5	-17	~ 0	7
A_{zzx}	~ 0	-11	~ 0	-4
$A_{xyy} = A_{yyx}$	~ 0	3	~ 0	-8
$A_{xzz} = A_{zxx}$	~ 0	-7	~ 0	-4

to be determined. We find, for the best fit, $\theta_0 = 2.5^\circ \pm 0.7^\circ$, $\sigma_\theta = 26^\circ \pm 5^\circ$, $\sigma_\phi = 27^\circ \pm 5^\circ$, and $\sigma_\psi = 35^\circ \pm 5^\circ$. These values, when used with Eq. (8) in Eq. (5) to calculate $(A_q)_{ijk}$, reproduce almost all the measured $(A_q)_{ijk}$ values within the experimental error, as shown in Table I.

The above result shows how the CH_2 groups are oriented on the rubbed PVA surface. Accordingly, we know that the PVA chains are well aligned along the rubbing direction with a fairly narrow angular spread, and on average, a $\sim 2.5^\circ$ backward tilt. One may notice that the number of $(A_q)_{ijk}$ used in this calculation far exceeds the number of parameters to be determined. The fact that we can still consistently reproduce all the measured $(A_q)_{ijk}$ values indicates that Eq. (8) is indeed a good representation of the orientational distribution of CH_2 .

From the known distribution function, we can calculate the orientational order parameter, usually defined as $S = \langle \frac{3}{2} (\hat{\xi} \cdot \hat{\xi}_0)^2 - \frac{1}{2} \rangle$, for the PVA chains, where $\hat{\xi}$ and $\hat{\xi}_0$ are the unit vectors denoting the local and average chain directions, respectively. We obtained $S = 0.52$. To see how this rubbed PVA surface induces LC alignment, we deposited a monolayer of LC molecules, octyl-cyanobiphenyl (8CB), on it and measured the orientational distribution of the LC monolayer using optical second harmonic generation [15]. We then calculated the orientational order parameter of the LC monolayer from the distribution and found it to be $S_{\text{LC}} = 0.54$. This suggests that the LC monolayer interacts strongly with the PVA surface and adopts an orientational ordering close to that of the underlying PVA chains. As demonstrated in Ref. [5], the orientation and alignment of the surface LC monolayer then governs completely the orientation and alignment of the entire LC film via molecular correlation.

In conclusion, we have demonstrated that SFG vibrational spectroscopy permits quantitative determination of orientational distribution for polymer molecular units at a surface. Application to a rubbed PVA surface enables us to have a detailed understanding of how rubbed polymer surfaces can induce bulk homogeneous alignment of LC

films. The technique should also be useful for studies of other relevant polymer interfacial problems.

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