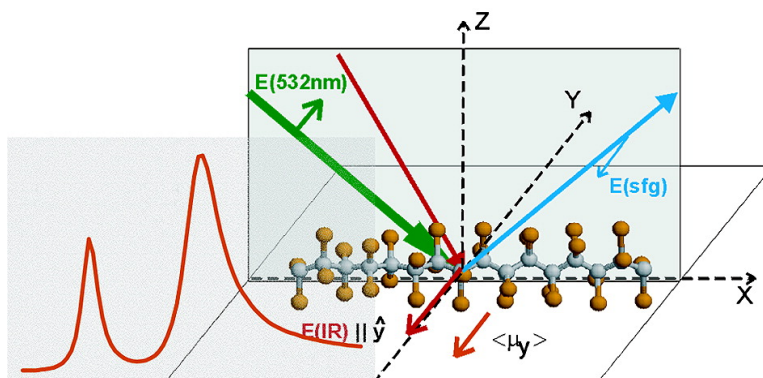## Communication

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Shear-Aligned Poly(tetrafluoroethylene) Films

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Surface Vibrational Spectroscopy on Shear-Aligned Poly(tetrafluoroethylene) Films

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Teflon or poly(tetrafluoroethylene) (PTFE, C_nF_{2n}) is well-known for its remarkable surface properties. Recently, it was found that highly oriented PTFE thin films could be rubbed onto a substrate by shearing a hot piece of PTFE. They can be used as templates to orient biological molecules,[1] organic films, and crystals, as well as polymers deposited on them.[2] Various mechanisms such as epitaxy,[3] graphoepitaxy,[4] and topographical induction[5] have been proposed to explain the surface-induced ordering effect. Clearly, for basic understanding of the effect, one needs to know the surface structure of the films at the molecular level. Transmission electron microscopy, X-ray diffraction, atomic force microscopy, and high-resolution electron energy loss spectroscopy have been used to study such films, but they are generally not sufficiently surface specific or sensitive to provide much detailed information about the surface structure.[6] In this context, sum-frequency vibrational spectroscopy (SFVS) is an ideal tool. It is highly surface specific and sensitive to a surface monolayer. The polarization-dependent surface vibrational spectra allow deduction of information about orientations of different functional groups. The technique has been successfully employed to probe surfaces of polymers with stretch modes in the CH_x and CO ranges.[7] In this communication, we report our findings from a study of surface structure of shear-deposited PTFE films using SFVS. The observed PTFE spectra are the first surface vibrational spectra ever obtained in the CF stretch region. From the spectra of different sample orientations and input and output polarization combinations, we find that the PTFE chains are well-aligned on the surface along the shearing direction. With the help of selection rules, the vibrational spectra associated with the well-aligned PTFE chains enable us to properly identify the vibrational modes of PTFE, helping to resolve the long-standing controversy over their assignment.[8]

The theory of SFVS has been described elsewhere.[9] The SF signal at ω_s generated in reflection from overlapping two input beams at ω_1 and ω_2 on a surface is proportional to $|\overset{\leftrightarrow}{\chi}_{\text{eff}}^{(2)}|^2$, where $\overset{\leftrightarrow}{\chi}_{\text{eff}}^{(2)}$ is the effective second-order surface nonlinear susceptibility defined as

$$\overset{\leftrightarrow}{\chi}_{\text{eff}}^{(2)} = [\hat{e}_s \cdot \overset{\leftrightarrow}{L}(\omega_s)] \cdot \overset{\leftrightarrow}{\chi}^{(2)} : [\overset{\leftrightarrow}{L}(\omega_1) \cdot \hat{e}_1][\overset{\leftrightarrow}{L}(\omega_2) \cdot \hat{e}_2]$$

$$\overset{\leftrightarrow}{\chi}^{(2)} = \overset{\leftrightarrow}{\chi}_{\text{NR}}^{(2)} + \sum_q \frac{\vec{A}_q}{\omega_2 - \omega_q + i\Gamma_q}$$

In the above expression, $\hat{e}_i$ and $\vec{L}(\omega_i)$ denote the unit polarization vector and the Fresnel coefficient of the field at ω_i at the surface, $\overset{\leftrightarrow}{\chi}_{\text{NR}}^{(2)}$ is the nonresonant background contribution to the nonlinear susceptibility, $\vec{A}_q$, ω_q, and Γ_q are the amplitude, resonant frequency, and damping constant of vibrational mode q, respectively, and we have assumed that the incoming frequency ω_2 is near resonance with the vibrational modes. Under the electric-dipole approximation, the nonlinear susceptibility vanishes in media with inversion symmetry but is nonzero at surfaces because of the broken

symmetry. The vibrationally resonant sum-frequency generation can be visualized as the combination of an infrared transition followed by an anti-Stokes Raman process. In terms of vibrational transition dipole moment $(\hbar/2\omega_q)^{1/2}(\partial\mu/\partial Q_q)$ and Raman polarizability $(\hbar/2\omega_q)^{1/2}(\partial\overset{\leftrightarrow}{\alpha}/\partial Q_q)$, we can write

$$A_{q,ijk} = -\frac{N_S}{\epsilon_0 \hbar} \sum_{i'j'k'} \frac{\hbar}{2\omega_q} \frac{\partial\alpha_{i'j'}}{\partial Q_q} \frac{\partial\mu_{k'}}{\partial Q_q} \langle(i\cdot i')(j\cdot j')(k\cdot k')\rangle$$

where N_S is the surface density of molecules, i, j, and k refer to the lab coordinates and i', j', and k' to the molecular coordinates, Q_q denotes the normal coordinate of vibrational mode q, and the angular brackets represent an average over molecular orientations. This indicates that only modes that are both infrared and Raman active can be detected in SFVS.

The PTFE thin films were prepared by shearing a hot Teflon rod at 300 °C[10] against a clean fused silica substrate at 200 °C under constant pressure ($\sim5 \times 10^4$ Pa) and constant speed (~0.5 cm/s). They appeared to SFVS to have forward−backward symmetry along the shearing direction and hence the C_{2v} symmetry. Defining $\hat{z}$ to be along the surface normal and $\hat{x}$ along the shearing direction, we have the following nonvanishing surface susceptibility elements for the films:[11]

$$\chi_{xxz}^{(2)}, \chi_{yyz}^{(2)}, \chi_{zzz}^{(2)}, \chi_{xzx}^{(2)} \cong \chi_{zxx}^{(2)}, \chi_{yzy}^{(2)} \cong \chi_{zyy}^{(2)}$$

The experimental arrangement was the same as the one described earlier.[9] A visible beam at 18 800 cm^{-1} and an infrared beam tunable from 750 to 1300 cm^{-1}, generated from a picosecond Nd: YAG laser system and an optical parametric system, were overlapped on a PTFE film exposed to air. The SF signal in reflection was detected by a photodetector/gated integrator system after proper spatial and spectral filtering. The SFVS spectra were taken with the film oriented so that the shearing direction was either parallel (||) or perpendicular (⊥) to the plane of incidence. Different input and output polarization combinations were used: SSP (denoting S-polarized SF output, S-polarized visible input, and P-polarized infrared input) to deduce $\chi_{xxz}^{(2)}$ and $\chi_{yyz}^{(2)}$, SPS to deduce $\chi_{xzx}^{(2)}$ and $\chi_{yzy}^{(2)}$, and PPP to deduce the remaining $\chi_{zzz}^{(2)}$.[9] The spectra appeared to be remarkably simple. No spectral features were observed in any polarization combination except SPS in which two peaks at ω_q of 1142 and 1204 cm^{-1} and Γ_q of 5 and 12 cm^{-1}, respectively, appeared when the sample was in the || geometry, as shown in Figure 1.

The shear-deposited films had an average thickness of ~10 nm as seen by AFM.[6] One might wonder if the PTFE bulk[11] or PTFE/substrate interface would contribute to the observed SPS spectrum. As a test, we covered the PTFE surface by a BaF₂ window with a thin layer of CCl₄ in between. The CCl₄ layer had no absorption in the 1100−1300 cm^{-1} region, and yet the SFVS spectrum disappeared completely. It reappeared immediately after evaporation of
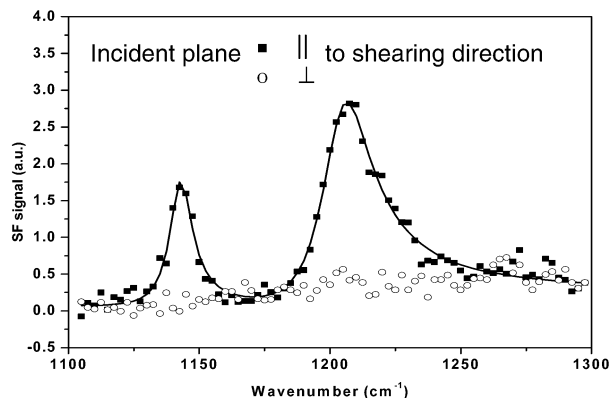
Figure 1. SFVS spectra from a shear-deposited thin film of PTFE. The polarization combination used was S (SFG), P (visible), and S (infrared).
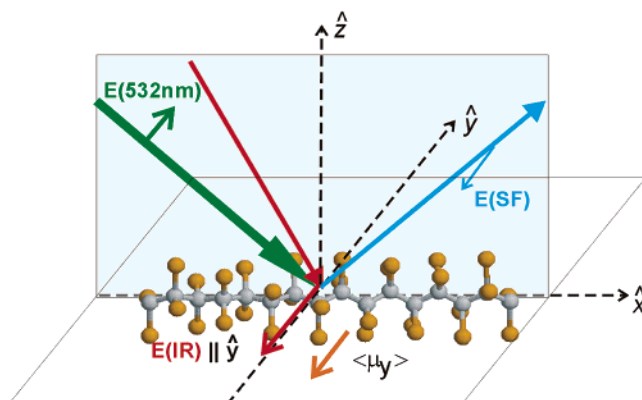

Figure 2. Schematic showing a PTFE chain aligned along the shearing direction in the incident plant. Electric field directions of the beams as marked are of SPS polarization combination.

CCl$_4$. Apparently, the CCl$_4$ liquid must have disrupted the ordered surface structure of PTFE and suppressed its SFVS spectrum. This indicates that the SF signal originated from the air/PTFE interface.

To understand the SFVS spectra and deduce information about the surface structure of the PTFE films, we follow the theoretical studies of vibrational modes of PTFE in the literature.[12] PTFE is a linear polymer of $[-(CF_2)-]_n$. Unlike polyethylene (C$_n$H$_{2n}$) which has a planar zigzag structure, PTFE chains have a 15$_7$ helical structure under room temperature in which 15 CF$_2$ groups are arranged along the helical axis in seven turns (but the films are racemic with equal number of right- and left-handed helices). Coupling between CF$_2$ groups along a chain is also stronger than CH$_2$, leading to normal vibrational modes that cannot be identified with individual CF$_2$ groups. Factor group analysis[13] for such a structure shows that its normal modes must have A$_1$, A$_2$, E$_1$, or E$_2$ symmetry; only the E$_1$ modes are both infrared and Raman active, and their infrared transition dipole is perpendicular to the helical axis. To excite the E$_1$ modes, one needs an infrared field component along the transition dipole. Now in our SFVS experiment on PTFE, vibrational modes were detected only with the SPS polarization combination and the ‖ geometry. Therefore, they must have their transition dipoles perpendicular to the shearing direction of the film. This, then, strongly suggests the following scenario. The PTFE chains must be well-aligned on the surface in the shearing direction (knowing that the bulk PTFE chains are well-oriented by shearing of the film[6]), and the vibrational modes observed in SFVS are of the E$_1$ symmetry as depicted in Figure 2. No other reasonable models can explain the experimental observation equally satisfactorily.

The fact that the vibrational modes appear only in the SPS and ‖ configuration indicates that among the five independent $\chi_{ijk}^{(2)}$ elements allowed by surface symmetry of the PTFE film, only $\chi_{yzy}^{(2)} \cong \chi_{zyy}^{(2)}$ is actually nonvanishing. This must result from intrinsic symmetry of the PTFE structure. That the vibrational modes have E$_1$ symmetry and the chains are aligned along the shearing direction makes $\chi_{xzx}^{(2)} = \chi_{zxx}^{(2)}$ vanish, but we still need to explain why $\chi_{xxz}^{(2)}$, $\chi_{yyz}^{(2)}$, and $\chi_{zzz}^{(2)}$ also nearly vanish. It can be shown[12] from group theory that for E$_1$ modes of a PTFE chain in space with 15$_7$ symmetry, the only allowed Raman polarizability elements are $\alpha_{y'x'} = \alpha_{x'y'}$ and $\alpha_{z'x'} = \alpha_{x'z'}$ where $\hat{x}'$ is along the chain. Having the chain oriented along $\hat{x}$ (such that $\hat{x}' = \hat{x}$), we must conclude from eq 1 that $\chi_{xxz}^{(2)}$, $\chi_{yyz}^{(2)}$, and $\chi_{zzz}^{(2)}$ as well as $\chi_{yzy}^{(2)}$ must all vanish. However, for surface PTFE chains, the symmetry breaking of $\hat{z}'$ versus $-\hat{z}'$ makes $\alpha_{y'z'} = \alpha_{z'y'}$ allowed. (This is similar to the differences between C$_{2v}$ and C$_2$ symmetry.) In this case, $\chi_{yzy}^{(2)}$ appears to be the only nonvanishing $\bar{\chi}^{(2)}$ element, as we have observed.

That we can conclude the observed PTFE vibrational modes at 1142 and 1204 cm^{-1} are of E$_1$ symmetry is interesting and meaningful. Ever since the early investigation nearly 50 years ago, the assignment of PTFE's vibrational modes has always been a matter of debate. IR and Raman spectroscopy on bulk PTFE generally reveal three modes around 1150, 1200, and 1240 cm^{-1} in the CF stretch range, but their assignment varies among different authors.[8] In our SFVS spectrum, the 1240 cm^{-1} mode is very weak and hardly distinguishable from the background noise. It indicates that the mode must be of symmetry other than E$_1$. Our results confirm the earlier assignment of this mode to be of A$_2$ symmetry by Peacock et al.[14] and Cutler et al.[15]

In conclusion, we have used SFVS to obtain the first surface vibrational spectra of PTFE films. The surprisingly simple spectra for the sheared films enable us to conclude that the helical PTFE chains are well-aligned on the surface along the shearing direction and the observed vibrational modes at 1142 and 1204 cm^{-1} are of the E$_1$ symmetry in agreement with some earlier analyses.

References

(1) Suzuki, H.; Oiwa, K.; Yamada, A.; Sakakibara, H.; Nakayama, H.; Mashiko, S. *Jpn. J. Appl. Phys., Part 1* **1995**, *34*, 3937.
(2) Wittman, J. C.; Smith, P. *Nature (London)* **1991**, *352*, 414.
(3) See, for example, Damman, P.; Dosiere, M.; Smith, P.; Wittmann, J. C. *J. Am. Chem. Soc.* **1995**, *112*, 1117.
(4) Smith, H. I.; Geis, M. W.; Thompson, C. V.; Atwater, H. A. *J. Cryst. Growth* **1983**, *63*, 527.
(5) Tanaka, T.; Ishitobi, M. *J. Phys. Chem. B* **2002**, *106*, 564.
(6) See, for example, (a) Fenwick, D.; Ihn, K. J.; Motamedi, F.; Wittmann, J. C. *J. Appl. Polym. Sci.* **1993**, *50*, 1151. (b) Dannetun, P.; Schott, M.; Rei Vilar, M. *Thin Solid Films* **1996**, *286*, 321. (c) Hansma H.; Motamedi, F.; Smith, P.; Hansma, P.; Wittman, J. C. *Polymer* **1992**, *33*, 647.
(7) Chen, Z.; Shen, Y. R.; Somorjai, G. A. *Annu. Rev. Phys. Chem.* **2002**, *53*, 437.
(8) See, for example, (a) ref 6b and references therein. (b) Masetti, G.; Cabassi, F.; Morelli, G.; Zerbi, G. *Macromolecules* **1973**, *6*, 700.
(9) Wei, X.; Hong, S. C.; Zhuang, X.; Goto, T.; Shen, Y. R. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2000**, *62*, 5160.
(10) Care should be taken to prevent the adverse environmental effects caused by thermolysis of PTFE upon heating. See, for example, Ellis, D. A.; Mabury, S. A.; Martin, J. W.; Muir, D. C. G. *Nature (London)* **2001**, *412*, 321.
(11) Wei, X.; Hong, S. C.; Lvovsky, A. I.; Held, H.; Shen, Y. R. *J. Phys. Chem. B* **2000**, *104*, 3349.
(12) Bower, D. I.; Maddams, W. F. *The Vibrational Spectroscopy of Polymers*; Cambridge University Press: New York, 1989.
(13) Moynihan, R. E. *J. Am. Chem. Soc.* **1959**, *81*, 1045.
(14) Peacock, C. J.; Hendra, P. J.; Willis, H. A.; Cudby M. E. A. *J. Chem. Soc. A* **1970**, 2943.
(15) Cutler, D. J.; Hendra, P. J.; Rahalkar, R. R.; Cudby, M. E. A. *Polymer* **1981**, *22*, 727.

JA037964L