

Molecular Orientation of Self-assembled Monolayer of Octadecanethiol on Platinum Surface Studied by Femtosecond Broad-bandwidth Sum Frequency Generation Spectroscopy

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The molecular orientation in self-assembled monolayer (SAM) of octadecanethiol (ODT) on platinum surface prepared in ethanol solution was examined by broad-bandwidth sum frequency generation (BB-SFG) spectroscopy. The bands attributed to the CH₃ symmetric and asymmetric stretching vibrational modes were observed in the SFG spectra. From the analysis of SFG intensity ratio of these two modes, the alkyl chain on platinum was found to be more perpendicular to the substrate than those on gold surface.

Self-assembled monolayers (SAMs) have been the subject of numerous studies¹ because of their potential applications in many fields such as biosensors, corrosion inhibition, wetting control, and biomolecular and electronic devices.^{2,3} Information about the structure and orientation of the SAMs is essential to develop new types of functional monolayer and to understand the fundamentals of electron-transfer behaviors at interfaces. There have been many studies of the self-assembly process and the structure of the SAM of alkanethiol by *in situ*^{4,5} and *ex situ*⁶ techniques. However, most of the studies reported so far are concerned with SAMs on gold surface. For wider applications of SAMs, construction and structural characterizations of SAMs on other metal surfaces are essential. For example, only few studies on the structure of SAMs on platinum surface have been reported^{7,8} and it was found that because of the strong affinity of platinum for oxygen, SAMs constructed on platinum surface are unstable and are much less ordered than those on gold surface.⁷

Sum frequency generation (SFG) spectroscopy is a powerful tool for the study of the molecular structures at interfaces. It has an advantage, over linear optical techniques, that it can determine not only the orientation and conformational orders but also lateral order and symmetry of molecular layers at surfaces.^{9–12} Recently, broad-bandwidth sum frequency generation (BB-SFG) spectroscopy, in which a broad-bandwidth IR pulses are mixed with a narrow-bandwidth visible pulses, has been demonstrated to be a powerful probe to provide structural information of molecular layer on solid surfaces in very short measurement time.

In this paper, we studied the assembly process of octadecanethiol (ODT) SAMs on platinum surface in ethanol solution by *ex situ* BB-SFG spectroscopy. The orientation angle of the methyl group was estimated using the ratio of the intensities of CH₃ symmetric and asymmetric stretching vibrational modes.

Figure 1 schematically shows the arrangement of BB-SFG system used in the present study. The details of the system will be described elsewhere.¹³ Briefly, The loosely focused visible (10 ps duration, 10 cm⁻¹ bandwidth, 0.1 μJ/pulse energy) and broad-bandwidth IR (100 fs duration, 200 cm⁻¹ bandwidth, 0.1 μJ/pulse energy) beams were overlapped at a sample surface.

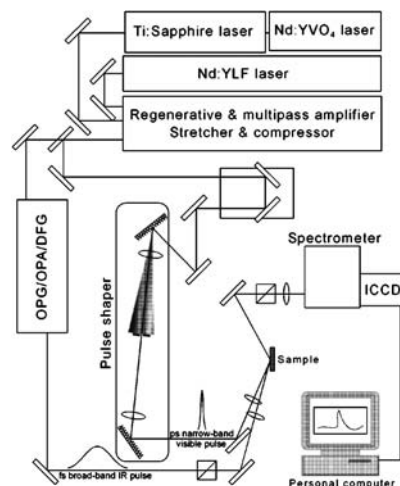


Figure 1. Schematic diagram of the femtosecond BB-SFG spectroscopy system used in this study.

The incident angles of the visible and IR were about 65 and 50 degrees, respectively. The SF light generated from the sample surface was detected by a spectrograph (Oriol Instruments, MS-257) and an ICCD multichannel detector (Andor, *iStar*). The SFG spectrum was obtained by dividing the ICCD output of the sample by that of GaAs. In the present experiment, polarization of the SFG, vis, and IR beams to obtain SFG spectra were p, p, and p, respectively, and SFG spectra were analyzed by using the following equation:¹⁴

$$I_{\text{SFG}} = \left| \chi_{\text{NR}}^{(2)} + \frac{A_0 e^{i\varphi}}{\omega - \omega_0 + i\Gamma_0} \right|^2, \quad (1)$$

where ω is the infrared frequency, $\chi_{\text{NR}}^{(2)}$ is the nonresonant contribution to the surface nonlinear susceptibility, and ω_0 , A_0 , f , and Γ_0 are the resonant frequency, transition amplitude, phase difference between resonant and nonresonant term and homogeneous width, respectively.

The substrates were prepared by sputtering Ti (5 nm) as an adhesive layer followed by Pt (25 nm) on a glass substrate. Platinum substrates were placed in a glass vessel containing 0.1 mM ODT ethanol solution (degassed with Ar) at room temperature for various time durations. The samples were rinsed with ethanol and dried with a stream of N₂.

Figure 2 shows the SFG spectra obtained after immersing the platinum substrate for (a) 1, (b) 3, (c) 4, and (d) 24 h. SFG spectra obtained after immersing a vacuum-evaporated gold on a glass substrate for 24 h is shown in Figure 2e for comparison. The solid lines were the results of least-squares fit using Eq 1. Five peaks observed at 2873, 2963, 2933, 2853, and 2915 cm⁻¹ can be assigned to CH₃ symmetric vibrational mode (ν^+), CH₃ asymmetric vibrational mode (ν^-), Fermi resonance

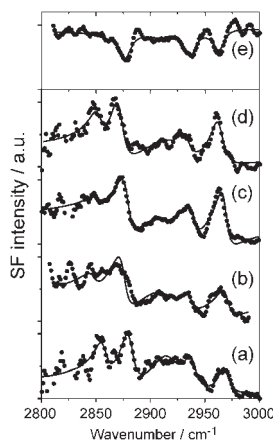


Figure 2. SFG spectra of ODT SAM on platinum (filled circle) prepared by the immersion of (a) 1 h, (b) 3 h, (c) 4 h, (d) 24 h and of (e) ODT SAM on gold prepared by the immersion of 24 h and fitted curve (full line) using Eq 1.

between r^+ and the overtone of the CH_3 bending (r^+_{FR}), CH_2 symmetric vibration, and CH_2 asymmetric vibration, respectively.¹⁵ If the alkyl chain has all trans conformation, it is well known that the methylene vibrational modes do not appear in the SFG spectra.^{15,16} The presence of the peaks at 2853 and 2915 cm^{-1} suggests that the alkanethiol SAMs on platinum surface were less ordered even after 24 h immersion time (Figure 2d) than those on gold¹¹ (Figure 2e) and silver.¹⁷ Since there was no increase of peak intensity of SFG spectra after 24 h immersion time, we can conclude that saturation coverage of ODT monolayer was attained at 24 h.

The ratio of the vibrational intensity of $A(r^+)$ and $A(r^-)$ was used to analyze the orientation of ODT SAMs on the platinum surface. By assuming an azimuthally isotropic interface, the ratio of the vibrational intensities of $A(r^+)$ and $A(r^-)$ can be approximated by¹⁸

$$\left| \frac{A(r^-)}{A(r^+)} \right| = \frac{\beta_{\text{caa}}}{\beta_{\text{aac}}} \times \frac{(2F_{\text{zzz}} - F_{\text{xxz}})(\cos\theta - \cos^3\theta)}{\left(F_{\text{zzz}} + \frac{F_{\text{xxz}}}{2} \left(1 + \frac{\beta_{\text{ccc}}}{\beta_{\text{aac}}} \right) \cos\theta - \left(F_{\text{zzz}} - \frac{F_{\text{xxz}}}{2} \right) \left(1 - \frac{\beta_{\text{ccc}}}{\beta_{\text{aac}}} \right) \cos^3\theta \right)}, \quad (2)$$

where θ is the angle between the main axis of the methyl group and the surface normal, F_{zzz} , F_{xxz} are the combination of Fresnel factors for the SFG, vis, and IR beams. The ratio for $\beta_{\text{cca}}/\beta_{\text{aac}}$ and $\beta_{\text{ccc}}/\beta_{\text{aac}}$ was 0.25 and 4.21, respectively.¹⁸

Figure 3 shows the dependence of the ratio of the vibrational intensities of $A(r^+)$ and $A(r^-)$ as a function of tilt angle calculated by using Eq 2. The ratio of $A(r^+)$ and $A(r^-)$ of the SFG spectrum after 24 h immersion in ODT ethanolic solution was 1.36 and the tilt angle of methyl group was determined to be ca. 37 deg. From this result, the tilt angle of the alkyl chains in the SAMs formed on platinum surface was estimated to be less than 5 deg from the surface normal. A plausible reason for such a small tilt angle is as follows. Less stable SAMs on platinum surface than on gold surface⁷ suggest that Pt-S bond is weaker than Au-S bond. The less strong interaction between SAM and substrate makes the interchain interactions more important, resulting the alkyl chains to be packed with more perpendicular orientation. However, since only limited information is available at present to discuss the details of the SAMs structure, further detailed investigation is required.

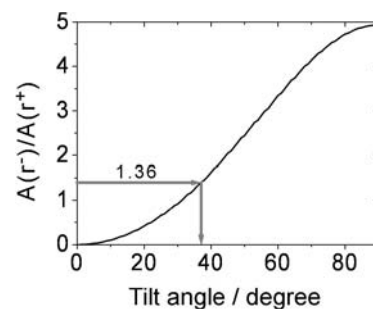


Figure 3. Calculated curves of $A(r^-)/A(r^+)$ vs the methyl angle from surface normal.

In summary, BB-SFG spectroscopy was used to study the assembly of ODT SAMs on platinum surface from ethanol solution. The orientation angle of the methyl group was estimated using the ratio of the intensities of CH_3 symmetric and asymmetric stretching vibrational modes. The alkyl chain on platinum was found to be more perpendicular to the substrate than those on gold surface.

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