

Orientation of *o*-, *m*-, and *p*-Methylbenzylmercaptans Adsorbed on Au(111) Probed by Broad-Bandwidth Sum Frequency Generation Spectroscopy

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Abstract

The molecular orientation in self-assembled monolayers of ortho, meta, and para isomers of methylbenzylmercaptans (OMBM, MMBM, and PMBM, respectively) on Au(111) has been studied using broad-bandwidth sum frequency generation spectroscopy and cyclic voltammetry. Cyclic voltammograms for the reductive desorption suggest that all methylbenzylmercaptans form closely packed monolayers. Sum frequency vibrational spectra for OMBM, MMBM and PMBM show the CH₃ symmetric stretching vibration mode. The vibrational intensities are greatest in PMBM and smallest in OMBM, implying the difference in the orientation of the methyl group. The vibrational intensities are compared with the hyperpolarizabilities of methylbenzylmercaptans from a calculation based on the density functional theory. OMBM molecules adsorb on Au(111) tilting their benzyl moieties so that the direction of the methyl group is parallel with the surface, whereas MMBM and PMBM molecules adsorb on Au(111) with their benzyl moieties being perpendicular to the surface.

1 Introduction

The adsorption and orientation of aromatic thiols have been studied over a decade for those with phenyl,^{1–28} biphenyl,^{4, 6, 10, 26, 29–37} terphenyl,^{4, 26, 38–41} naphthalene,^{12, 29, 42} and heteroaromatic moieties,^{6, 15, 23, 43, 44} in view of their unique properties that alkanethiols do not have, such as rigidity,^{14, 25} electronic conductivity,^{9, 41, 45, 46} and electrochemical properties.^{8, 11, 43, 44}

The surfaces of thiol-covered gold can be functionalized by introducing a functional group to the thiols. The orientation of the group as well as its nature and surface density is important to control the physicochemical properties of the surfaces. There has been several reports which tried to change the orientation of the functional groups by changing their substituent positions to aromatic thiols.^{17, 22, 25, 27} Pradeep *et al.* reported that *o*- and *p*-chlorobenzylmercaptan SAMs on gold differ in the reactivity with Cr⁺ and Cr-containing cations.¹⁷ They concluded that the chlorine atom of the former isomer is buried in the SAM whereas that of the latter is exposed to the SAM surface. Their results were later confirmed by a metastable impact electron spectroscopic study.²⁷ Batz *et al.* investigated *o*-, *m*- and *p*-aminothiophenol SAMs on gold using electrochemistry and surface tunneling microscopy, and suggested that these isomers are oxidized to different products at the gold surfaces due to the different orientation and density of amino groups.²² These authors suggested that their aromatic moieties (i.e. benzyl moiety and phenyl moiety, respectively) are perpendicular to the surfaces irrespective of the position of the functional groups. It is expected, however, that the position of the functional groups can affect the orientation of the aromatic moieties due to the change in the interaction between the adsorbed molecules.

In the present paper, we will report the *o*-, *m*-, and *p*-substituent effect on the orientation of methylbenzylmercaptans on Au(111) using broad-bandwidth sum frequency generation (BBSFG).^{47, 48} We will show that the orientation of benzylmercaptans is affected by the position of the methyl group due to the different degree of the repulsive interaction between adsorbed molecules that are closely packed in the SAMs irrespective of the position of the methyl group.

2 Experimental

Materials. Benzylmercaptan (BM, Wako), *o*-methylbenzylmercaptan (OMBM, Avocado Research Chemicals), *m*-methylbenzylmercaptan (MMBM, Lancaster Synthesis), and *p*-methylbenzylmercaptan (PMBM, Avocado Research Chemicals) were used without further purification. The substrates with the thiol SAM on Au(111) were prepared as described elsewhere.⁴⁹ Gold was vapor-deposited on a freshly cleaved mica surface at 850 K at less than 1.3×10^{-3} Pa. The mica substrates were annealed at 800 K for 8 h before use. The substrates were then immersed in the 1×10^{-3} mol dm⁻³ ethanol solution of one of benzylmercaptans at least 24 h.

BBSFG system. The system for BBSFG was the same as that described elsewhere.⁵⁰ Briefly, broad-bandwidth IR pulses (duration-150 fs, bandwidth-200 cm⁻¹, energy-1.5 μ J/pulse) and narrow-bandwidth visible pulses (duration-10 ps, bandwidth-12 cm⁻¹, energy-2.5 μ J/pulse) were made coaxial using a dichroic mirror and were introduced to the thiol-covered gold surface at the incident angle of 60°. Both IR and visible pulses are *p*-polarized and *p*-polarized component of sum-frequency (SF) light was analyzed: *ppp*-polarization (*p*-SF, *p*-vis, *p*-IR). The SF light with broad bandwidth was dispersed by a monochromator and was detected by a CCD. Typical time to obtain one spectrum was 20 min and the spectra shown here were averaged for 3-4 samples.

Cyclic voltammetry. Cyclic voltammograms (CVs) for the reductive desorption of benzylmercaptans from gold surface were recorded in 0.5 mol dm⁻³ KOH using an Ag/AgCl/saturated KCl electrode as the reference electrode and a platinum wire as the counter electrode. The thiol-covered gold substrate was mounted at the bottom of a cone-shaped cell. The area of the electrode surface was 0.126 cm². The solution was deaerated by bubbling Ar gas for 10 min.

3 Results and Discussion

Voltammetric properties of benzylmercaptans. Figure 1 shows CVs for the reductive desorption of BM, OMBM, MMBM and PMBM. Regardless of a kind of benzylmercaptans, a single reduction peak was observed. In Table 1 are summarized obtained parameters: peak potential (E_p), full width of half maximum (FWHM) of the peak, and charge density (q) calculated from the peak area. The values of E_p for BM, OMBM and MMBM were -809, -815 and -792 mV, respectively. On the other hand E_p of PMBM was -853 mV, which was more negative than the others. Since E_p primarily reflects the difference between the Gibbs energy of the thiols in the solution and that at the surface, the more negative E_p of PMBM may result from the lower solubility in the solution⁵¹ and/or the stronger attractive interaction between adsorbed molecules at the surface.⁴⁹ The FWHM was ~ 30 mV at the scan rate of 20 mV s^{-1} , which is close to that of closely packed octanethiol SAMs on Au(111).⁴⁹ The values of q were $\sim 110 \text{ C cm}^{-2}$ for all benzylmercaptans, which is $\sim 40\%$ greater than 77 C cm^{-2} expected for the closely packed $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of thiols on Au(111). This discrepancy is probably due to the fact that q contains the contribution from the double-layer charging current due to the change in the capacitance at the electrode during the desorption of adsorbates. Our previous work suggests that it can reach one-third of the total charge.⁴⁹ The q values for benzylmercaptans obtained above suggest that all monolayers of benzylmercaptans are closely packed to the density similar to that predicted by the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure.

SF vibrational spectra of benzylmercaptans. Figure 2(a) shows the SF vibrational spectrum in the CH vibration region for BM on Au(111). The solid line is calculated by a least-square fitting of a model function to the experimental data. The model function we employed is:⁵⁰

$$I_{\text{sf}}(\omega_{\text{ir}}) = |\chi_{\text{tot}}|^2 \times \left(\sum_n a_n \exp \left[-\frac{(\omega_{\text{ir}} - \omega_n)^2}{2\gamma_n^2} \right] \right) \quad (1)$$

where I_{sf} is the intensity of the SF light, ω_{ir} is the angular frequency of IR pulses, χ_{tot} is the total second-order susceptibility of the surface, and the parameters for broad-bandwidth IR envelope, a_n , ω_n , and γ_n , are the amplitude, the angular frequency, and the bandwidth

of n -th Gaussian function, respectively. The fact that the IR envelope can be decomposed to the sum of the Gaussian functions is likely to be caused by the multiple phase matching condition occurring at the nonlinear crystal for the wavelength conversion of the IR pulses.⁵⁰ The susceptibility χ_{tot} is composed of the two components originating from gold and adsorbates, that is, the nonresonant component, $\chi_{\text{NR}}^{(2)}$, and the resonant components, $\chi_{\text{R},\nu}^{(2)}$, for a vibrational mode, ν , respectively.^{52, 53}

$$\chi_{\text{tot}} = \chi_{\text{NR}}^{(2)} + \sum_{\nu} \chi_{\text{R},\nu}^{(2)} e^{i\phi_{\nu}} \quad (2)$$

$$= \chi_{\text{NR}}^{(2)} \left[1 + \sum_{\nu} \frac{A_{\nu} e^{i\phi_{\nu}}}{\omega_{\text{ir}} - \omega_{\nu} + i\Gamma_{\nu}} \right] \quad (3)$$

where A_{ν} , ϕ_{ν} , ω_{ν} , and Γ_{ν} are the amplitude, the phase difference, the angular frequency, and the bandwidth of the Lorentzian function for ν , respectively. Here A_{ν} has been normalized by $\chi_{\text{NR}}^{(2)}$. Figures 2(b) and 2(c) show the broad-bandwidth IR envelope and χ_{tot} , respectively. The vibrational intensity for ν , V_{ν} , may be defined as follows:⁵⁴

$$\begin{aligned} V_{\nu} &\equiv \left| \frac{\chi_{\text{R},\nu}^{(2)}(\omega_{\text{ir}} = \omega_{\nu})}{\chi_{\text{NR}}^{(2)}} \right| \\ &= A_{\nu}/\Gamma_{\nu} \end{aligned} \quad (4)$$

In the spectrum of BM, the only one dispersive dip appears at 3060 cm^{-1} . We assigned this to ν_2 , which is one of the ring CH stretching vibrational modes in the Wilson's notation for benzene-derivatives.⁵⁵ Since ν_2 has a transition dipole moment parallel to the main axis of the benzyl moiety, the strong intensity for ν_2 accords with the results of the previous works that aromatic methanethiols such as benzylmercaptans,^{10, 19} biphenylmethanethiols,¹⁰ terphenylmethanethiols,³⁹ form closely packed monolayers with their orientation perpendicular to the gold surface. Other ring CH stretching modes are not discerned. Yeganeh *et al.* reported the small signal of ν_{7a} (3053 cm^{-1}) and ν_{7b} (3027 cm^{-1}) as well as the large signal of ν_2 (3068 cm^{-1}) in the SF vibrational spectra for polystyrene surface at ppp-polarization condition.⁵⁶ They also measured the SF vibrational spectra for ssp- and sps-polarization conditions, and the signal of ν_{7a} and ν_{7b} seems to be mainly originated from $\chi_{\text{R},xxz}$ and $\chi_{\text{R},zxx}$ components, respectively.⁵⁶ Here the subscript ijk indicates the i component of the induced second-order polarization, and the j and k components of

the electric field of the IR and visible pulses on surfaces, respectively.⁵² In our case of gold surface, the $\chi_{R,zzz}$ component overwhelms others due to the very weak magnitudes of the Fresnel coefficients in x and y directions; so called “surface selection rule” applies.⁵⁷ It seems thus reasonable that only ν_2 of the ring CH stretching vibrational modes appears in the spectrum of BM on Au(111). The CH₂ symmetric and asymmetric stretching modes are also not found, which are known to appear at 2931 and 2845 cm⁻¹ in the infrared spectra of the bulk liquid. The absence of these two modes in the SF vibrational spectra agrees with the orientation of BM molecules on the gold surface with their benzyl moieties perpendicular to the gold surface, so that the directions of the two transition moments are both parallel to the surface.

Figures 3, 4, and 5 show the SF vibrational spectra for OMBM, MMBM and PMBM, respectively. In these methylbenzylmercaptans, ν_2 cannot be discerned and two dips at 2866 and 2920 cm⁻¹ appears instead. These dips are clearly attributable to the CH₃ symmetric stretching vibrational mode, r^+ , that splits to two bands because of the Fermi resonance with the overtone of the CH₃ bending mode. The absence of ν_2 in the spectra of methylbenzylmercaptans may be due to the low IR intensity or Raman scattering activity for di-substituted benzenes. The CH₃ asymmetric stretching mode, r^- , is also not detected due to both its low IR intensity and Raman scattering activity when a methyl group is attached to a phenyl ring.⁵⁸ The depth of r^+ reflects the magnitude of the vibrational intensity, V . The greater the V , the smaller the methyl angle, θ , which is defined as the angle between the main axis of the methyl group and the surface normal. The depth of r^+ increased in the order of PMBM, MMBM, and OMBM, suggesting that θ is smallest in PMBM and greatest in OMBM.

Table 2 shows the values of the fitted parameters for ν_2 in the spectrum of BM and r^+ in the spectra of OMBM, MMBM and PMBM. The values of V for r^+ of OMBM, MMBM and PMBM were obtained from the fitting of the model function to the spectra. One notable feature in Table 2 is that the phase difference ϕ of r^+ is about the same for all methylbenzylmercaptans. This fact strongly indicates that ϕ remains unchanged even when the orientation of the methyl group is altered. This feature will be discussed below.

Comparison of V with β from DFT calculations for OMBM, MMBM and PMBM.

In our previous study of alkanethiol SAMs, the orientation of the methyl group was estimated using the ratio of the vibrational intensities for r^+ and r^- .⁵⁰ In the present case, however, we cannot use the same procedure because of the absence of r^- in the spectra. We calculated the hyperpolarizability for r^+ , β , to estimate θ from V and β using Gaussian 98 for the calculation based on the density functional theory (DFT) at the B3LYP/6-311+G** level.⁵⁹

The relationship between β and $\chi_{R,r^+,zzz}^{(2)}$, which is the dominant component of the second-order susceptibility for r^+ in our case,⁵⁷ is expressed as:⁶⁰

$$\chi_{R,r^+,zzz}^{(2)} = \frac{N_s \beta_{ccc}}{4\epsilon_0} [\langle \cos \theta \rangle (r + 3) - \langle \cos 3\theta \rangle (r - 1)] \quad (5)$$

where N_s is the number of molecules on the surfaces, ϵ_0 is the dielectric constant in vacuum, $r = \beta_{aac}/\beta_{ccc}$. The subscript ijk of β denotes the i component of the second-order dipole moment of the molecule induced by the j and k components of the electric field of the IR and visible pulses, respectively, and c axis is the main axis of the methyl group, a axis is parallel to the mirror plane of the methyl group assumed to have C_{3v} symmetry around the c axis, and b axis is the remaining axis perpendicular to both a and c axes.⁶¹ The component of hyperpolarizability, β_{ccc} , can be expressed as^{52, 62, 63}

$$\beta_{ccc} \propto \mu_{ng}^c M_{gn}^{cc} \quad (6)$$

where μ_{ng}^c is the c component of the IR transition moment from the ground state, g , to the vibrationally excited state, n , and M_{gn}^{cc} is the cc component of the Raman scattering transition moment from n to g . Here μ_{ng}^c and M_{gn}^{cc} are proportional to the square root of the IR intensity and Raman scattering activity, A_{ir} and A_r , respectively.^{64, 65}

$$\mu_{ng}^c = |\vec{\mu}_{ng}| \propto \left| \frac{\partial \vec{\mu}}{\partial Q} \right| \propto (A_{ir})^{1/2} \quad (7)$$

$$M_{gn}^{cc} \propto \frac{\partial \alpha_{cc}}{\partial Q} \propto (A_r)^{1/2} \quad (8)$$

where $\vec{\mu}$ is the dipole moment, Q the normal coordinate, and α the polarizability of the molecule. To derive the right hand side of eq 8, we used the relationship that the nonvanishing components of the polarizability tensor are $\alpha_{aa}(= \alpha_{bb})$, α_{cc} and $(\partial \alpha_{aa}/\partial Q)/(\partial \alpha_{cc}/\partial Q)$

= r . From eqs 6-8, we obtain

$$\beta_{ccc} \propto (A_{ir}A_r)^{1/2} \quad (9)$$

A value of β can be estimated from A_{ir} and A_r values calculated by DFT. Here we assumed that some of these quantities are positive values, though this assumption does not affect the orientation analysis described below. We also evaluated the unperturbed vibrational intensity for r^+ , $V_{r_u^+}$, from the vibrational intensities of the two bands, $V_{r_1^+}$ (2920 cm^{-1}) and $V_{r_2^+}$ (2866 cm^{-1}),⁶⁶ using the relationship that was used to calculate the unperturbed IR intensity from that of split bands.⁶⁴

$$V_{r_u^+} = (V_{r_1^+}^2 + V_{r_2^+}^2)^{1/2} \quad (10)$$

Equation 10 was derived from two equations, $\mu_{n_0g}^c{}^2 = \mu_{ng}^c{}^2 + \mu_{mg}^c{}^2$ and $M_{gn_0}^{cc}{}^2 = M_{gn}^{cc}{}^2 + M_{gm}^{cc}{}^2$ where n_0 is the unperturbed vibrationally excited state, and n and m are the split excited states, assuming that the cross terms of $\mu_{ng}^c M_{gm}^{cc}$ and $\mu_{mg}^c M_{gn}^{cc}$ were negligible.

By using eqs 4, 5, and 10, we estimated θ for methylbenzylmercaptans on Au(111). We assumed that $r = 1$ for all methylbenzylmercaptans as our previous report on the SAMs of alkanethiols on Au(111).⁵⁰ We further made three assumptions for evaluating θ : a uniform value of N for all benzylmercaptans, no angular distribution of θ , and $\theta = 0^\circ$ for PMBM. The third assumption is supported by the IR-reflection absorption (RA) spectra for PMBM and BM, in which the intensity of the vibrational bands except for that parallel to the molecular main axis is negligible.⁶⁷ Wöll *et al.* also found the negligible intensity of the vibrational bands in IR-RA spectra for terphenylmethanethiol on gold surface.³⁹

Table 3 lists the estimated value of θ . Also shown is the angle, θ_e , that is defined as the expected θ when the benzyl moieties of methylbenzylmercaptans are perpendicular to the surface. For MMBM, θ was estimated to be 62° , which is close to θ_e , 60° . We assumed that the tilt angle in the out-of-plane direction of the benzyl moieties is negligible because the tilt in this direction considerably decreases the density of molecules and contradicts with the closely packed structure. From this assumption and $\theta \approx \theta_e$, the benzyl moiety of MMBM is likely to be perpendicular to the surface. On the other hand, the calculated values of θ for OMBM is 83° , which is considerably smaller than θ_e , 120° . This difference suggests that OMBM molecules tilt their benzyl moieties so that the direction of the

methyl group is parallel with the surface. The orientation for methylbenzylmercaptans emerged from the present orientation analysis is illustrated in Figure 6, assuming that the dihedral angle between the surface-S-C plane and the phenyl plane is 90° at which the repulsion between sulfur atom and phenyl moiety inside these molecules is minimum.

The orientation of the methyl group for the SAMs of methylbenzylmercaptans can also be inferred from ϕ shown in Table 2. The sign of $\chi_{R,r}^{(2)}$ changes depending on whether the methyl group points upward ($\theta < 90^\circ$) or downward ($\theta > 90^\circ$) on average with respect to the surface (*cf.* eq 5). The change in the sign of the $\chi_{R,r}^{(2)}$ is equivalent to the 180° (π rad.) inversion of ϕ because $e^{\pi i} = -1$. Ward *et al.* studied the $\chi_{R,r}^{(2)}$ of alkanethiol forming SAM on gold with the methyl group pointing upward and that of dodecanol on the SAM with the methyl group pointing downward, and showed that the phase of the former is 180° different from that of the latter.⁶⁸ In our case of OMBM, MMBM, and PMBM, the ϕ values are almost the same and are not 180° inverted with respect to each other. The same values of ϕ indicate that the methyl groups of all methylbenzylmercaptans point upward, or downward. From the geometrical consideration of PMBM, the methyl group of PMBM should point upward. Therefore the methyl group of OMBM and MMBM also point upward: $\theta < 90^\circ$. This finding illustrates one of the advantages of SFG, which IR and Raman spectroscopy do not have.

The position effect of the methyl group on the orientation of benzylmercaptans can be discussed in view of the van der Waals interaction between the adsorbed molecules. BM is known to form closely packed monolayers on gold with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure.¹⁰ The BM molecules seem to form so called “herringbone structure” with their benzyl moieties being perpendicular to the surface, similar to aromatic thiols with biphenyl and terphenyl moieties.^{4, 29} The SAM of PMBM is expected to have the same structure as that of BM because the interaction between the methyl groups in the para position is attractive and does not hinder the packing of the adsorbed molecules; the van der Waals radius of the methyl group is 3.9 Å,⁶⁹ which is smaller than the distance of 5 Å between adsorbed molecules in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. On the other hand, the OMBM and MMBM SAMs cannot take the same structure because of the repulsion

between the methyl groups and the neighboring benzyl moieties. This explains why the OMBM molecules adsorbed on gold tilt their benzyl moieties. The OMBM and MMBM SAMs are therefore likely to have structures in which the density of molecules is comparable to that of the ($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ structure but with different molecular orientations. A further study using IR-RAS and STM is in progress to assure the orientations and structures of benzylmercaptans.

4 Conclusion

The orientations of methylbenzylmercaptans adsorbed on Au(111) have been revealed by the combination of the reliable vibrational spectra using BBSFG with the orientation analysis including the DFT calculation. The position of the methyl groups of methylbenzylmercaptans seems to affect their molecular orientations and the structures on Au(111), although the packing density of molecules is at the same level for all methylbenzylmercaptans. The present results indicate the importance of the substituent position for functionalization of the SAM surface of aromatic-thiols by introducing the substituent.

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Table 1: Parameters obtained from CVs for the reductive desorption of benzylmercaptans on Au(111).

Molecule	E_p (mV)	FWHM (mV)	q ($\mu\text{C cm}^{-2}$)
BM	-809 $\pm$ 11	36 $\pm$ 6	122 $\pm$ 5
OMBM	-815 $\pm$ 9	27 $\pm$ 2	101 $\pm$ 5
MMBM	-792 $\pm$ 8	36 $\pm$ 9	114 $\pm$ 12
PMBM	-853 $\pm$ 16	30 $\pm$ 7	103 $\pm$ 7

Table 2: Fitted parameters for the bands in the SF vibrational spectra of benzylmercaptans on Au(111).

Molecule	Mode	A (cm^{-1})	ϕ (π rad.)	ν_0 (cm^{-1})	Γ (cm^{-1})	$V (=A/\Gamma)$
BM	$\nu_2^{a)}$	2.2	2.0	3060	4.7	0.48
OMBM	$r_1^{+b)}$	0.5	1.7	2920 ^{d)}	12.4 ^{d)}	0.04
MMBM	$r_1^{+b)}$	1.5	1.7	2920 ^{d)}	12.4	0.12
PMBM	$r_1^{+b)}$	3.5	1.9	2920 ^{d)}	10.5	0.33
OMBM	$r_2^{+c)}$	-	-	-	-	0.00 ^{e)}
MMBM	$r_2^{+c)}$	0.9	1.7	2866 ^{d)}	14.9	0.06
PMBM	$r_2^{+c)}$	4.2	1.7	2866 ^{d)}	21.0	0.20

a) One of the ring CH stretching modes.⁵⁵ b) and c) Two 2920 and 2866 cm^{-1} split bands of the CH_3 symmetric stretching mode, respectively. d) Fixed parameters. e) Noise level.

Table 3: The unperturbed vibrational intensity, the hyperpolarizabilities from the DFT calculations and the methyl angle of methylbenzylmercaptans.

Molecule	$V_{\text{r}_u^+}$	β	$V_{\text{r}_u^+}/\beta^a)$	θ	$\theta_e^b)$
		(a.u.)	(a.u.)	(degrees)	(degrees)
OMBM	0.04	146	0.12	83	120
MMBM	0.13	126	0.47	62	60
PMBM	0.39	170	1.00	0 ^{c)}	0

a) Normalized. *b)* Defined as the expected θ when the benzyl moieties are perpendicular to the surface. *c)* PMBM molecules are assumed to stand with their methyl groups being perpendicular to the surface.

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Figure captions

Figure 1. Cyclic voltammograms for the reductive desorption of BM, OMBM, MMBM, and PMBM. Scan rate is 20 mV s⁻¹.

Figure 2. (a) Sum frequency vibrational spectra (open circle) for BM SAM on Au(111) and fitted curves (solid line), (b) decomposed broad-bandwidth IR pulses, and (c) the total second-order susceptibility, $\chi_{\text{tot}}^{(2)}$, normalized by $\chi_{\text{NR}}^{(2)}$.

Figure 3. (a) Sum frequency vibrational spectra (open circle) for OMBM SAM on Au(111) and fitted curves (solid line), (b) decomposed broad-bandwidth IR pulses, and (c) the total second-order susceptibility, $\chi_{\text{tot}}^{(2)}$, normalized by $\chi_{\text{NR}}^{(2)}$.

Figure 4. (a) Sum frequency vibrational spectra (open circle) for MMBM SAM on Au(111) and fitted curves (solid line), (b) decomposed broad-bandwidth IR pulses, and (c) the total second-order susceptibility, $\chi_{\text{tot}}^{(2)}$, normalized by $\chi_{\text{NR}}^{(2)}$.

Figure 5. (a) Sum frequency vibrational spectra (open circle) for PMBM SAM on Au(111) and fitted curves (solid line), (b) decomposed broad-bandwidth IR pulses, and (c) the total second-order susceptibility, $\chi_{\text{tot}}^{(2)}$, normalized by $\chi_{\text{NR}}^{(2)}$.

Figure 6. Orientation of PMBM, MMBM, and OMBM adsorbed on Au(111).

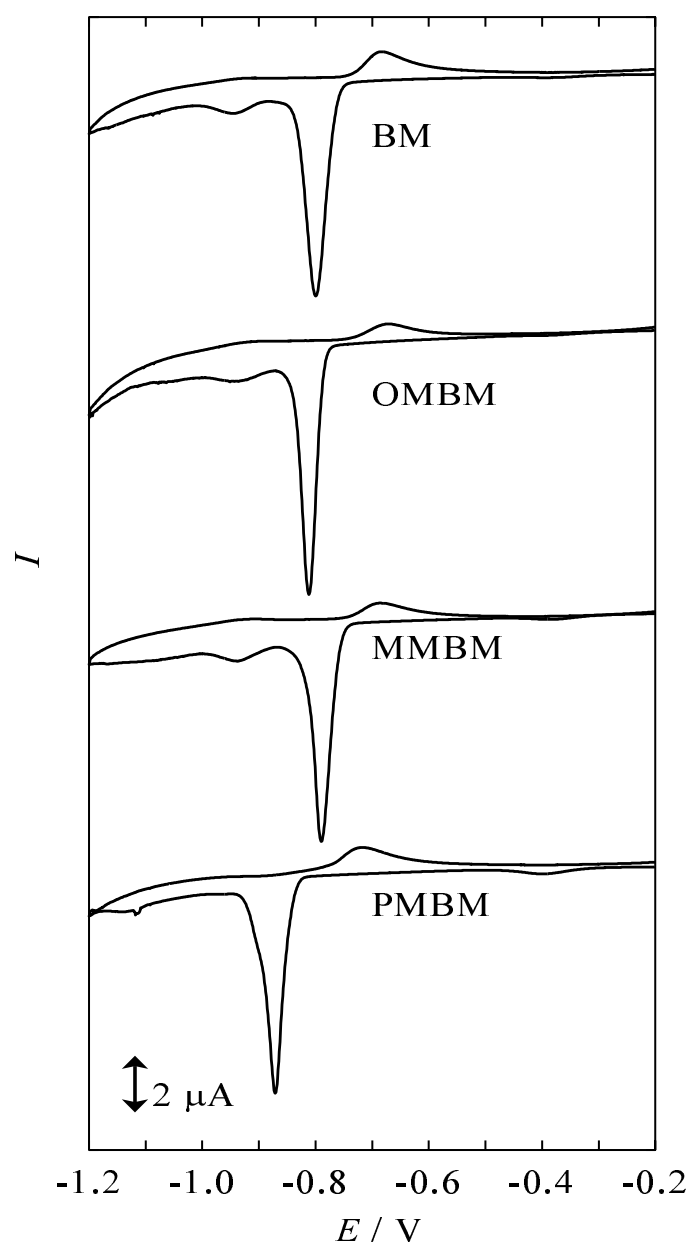


Fig. 1 (Nishi et al.)

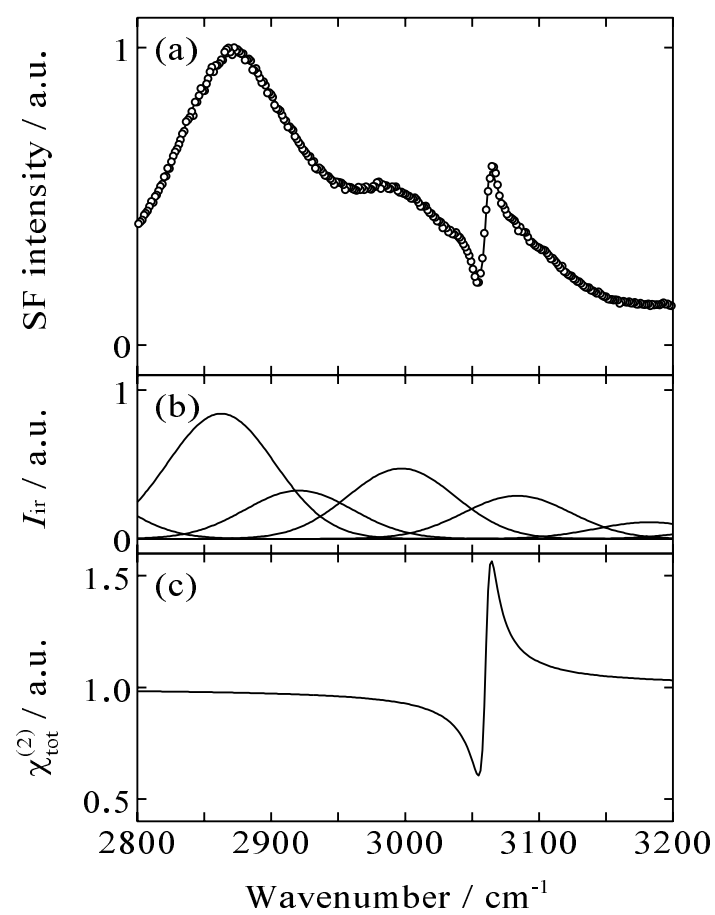


Fig. 2 (Nishi et al.)

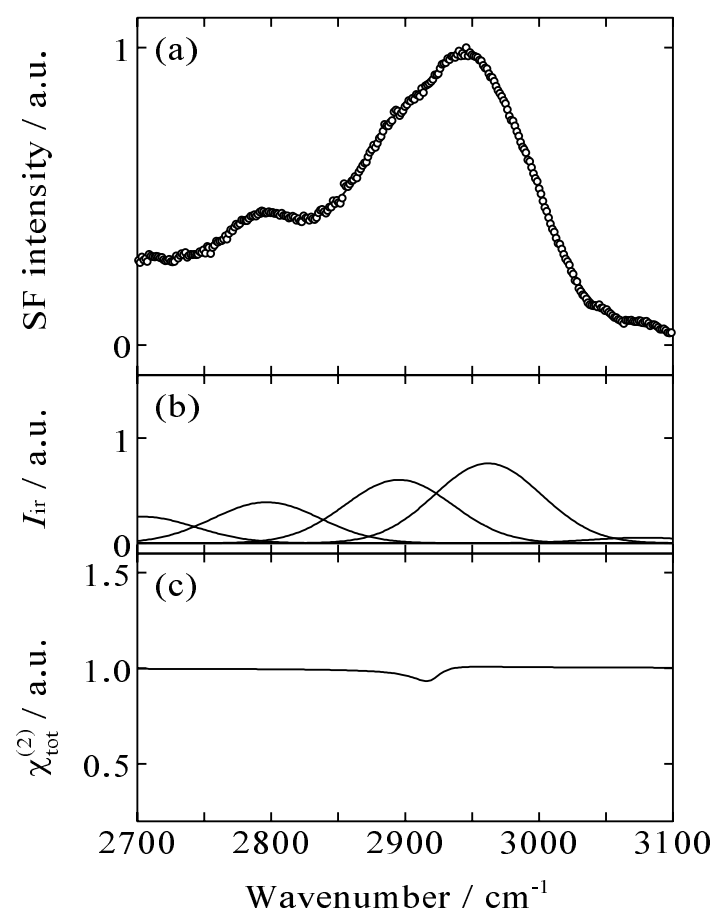


Fig. 3 (Nishi et al.)

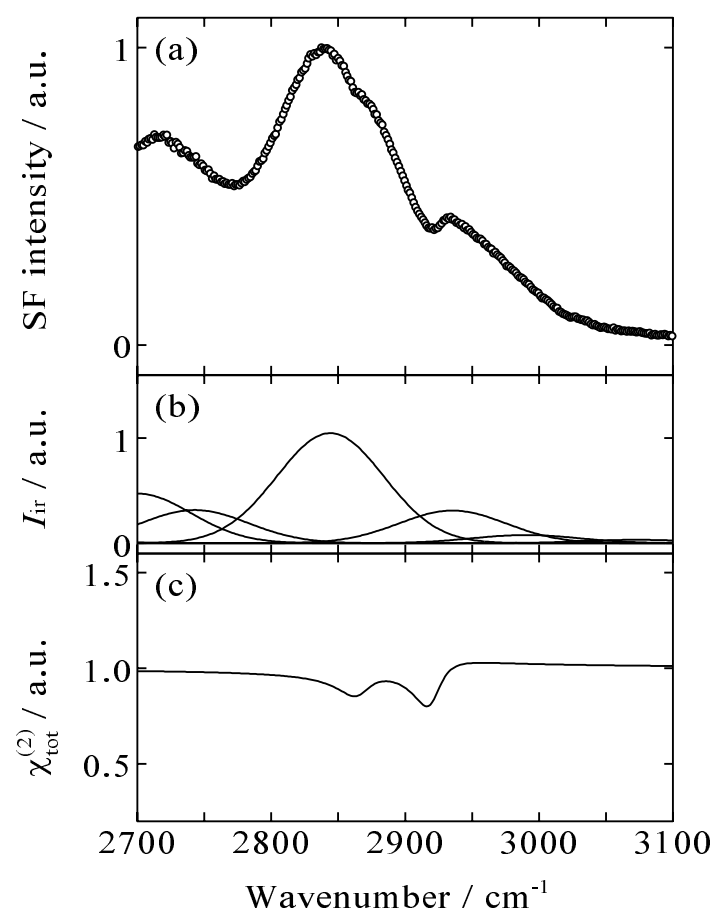


Fig. 4 (Nishi et al.)

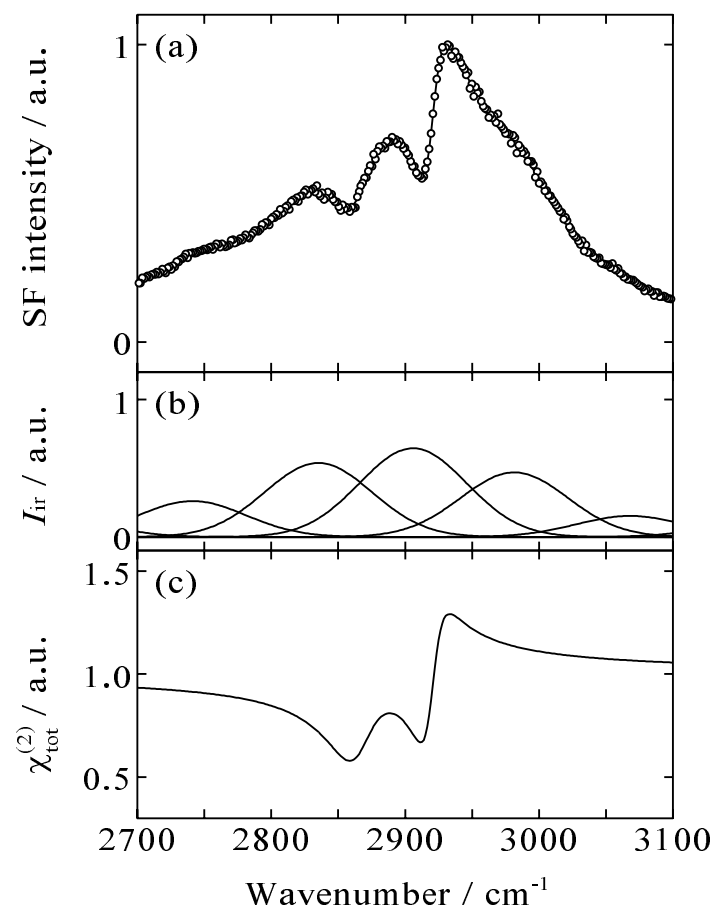


Fig. 5 (Nishi et al.)

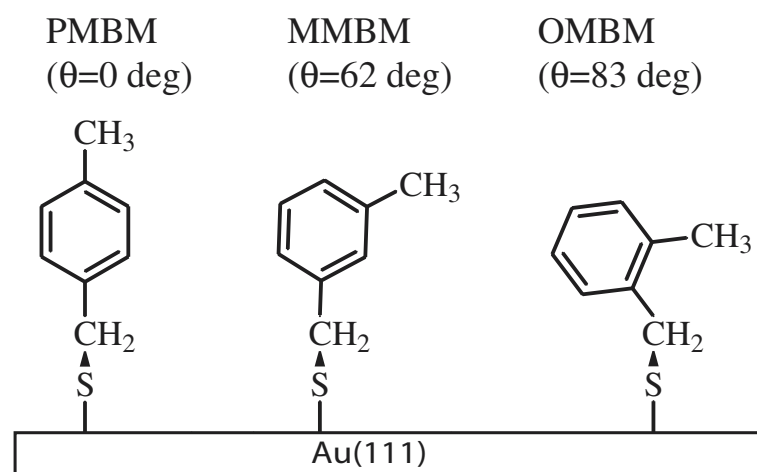


Fig. 6 (Nishi et al.)