Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Spectroscopic Evidence for the Origin of Odd-Even Effects in Self-Assembled Monolayers and Effects of Substrate Roughness

*Jiahao Chen[1,3,4†], Jian Liu[2,†], Ian D. Tevis[1], Richard S. Andino[2], Christina M. Miller[2], Lawrence D. Ziegler[2], Xin Chen[2] and Martin Thuo[1,4,5] **

[1]Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA

[2]Department of Chemistry and the Photonics Center, Boston University, Boston, MA 02215, USA

[3]Division of Materials Science and Engineering, Ames Laboratory, Ames, Iowa 50011

[4]Micro-electronic research center, Iowa State University, 133 Applied Sciences Complex I, 1925 Scholl Road, Ames, Iowa 50011 USA

[5]Biopolymer and Biocomposites Research Team, Center for Bioplastics and Biocomposites, Iowa State University, Ames, Iowa 50011 USA

Grain size and surface coverage calculation.

1. Open AFM image (with scale bar) in *ImageJ* and change it into 8-bit mode.
2. Use the threshed to tune the color of the image, checking with the scale bar to make sure only region within 1nm of the midline is black.
3. Process the image with watershed. Then use the inbuilt function in *ImageJ* to calculate the particle size and the surface coverage automatically for the image.

Fittings of SFG spectra

The intensity of sum-frequency generation (SFG) signal, I_{SFG}, can be expressed as

$$I_{SFG} \propto \left|\chi_{NR}^{(2)} + \sum_q \chi_q^{(2)}\right|^2 \cdot I_{800nm} \cdot I_{IR} \tag{1S}$$

where I_{800nm} and I_{IR} are the intensities of the incident 800 nm and IR beams. $\chi_{NR}^{(2)}$ and $\chi_q^{(2)}$ represent the complex second order susceptibilities of a non-resonant background term and the vibrationally resonant sum frequency term, respectively. The resonant vibrationally resonant term, $\chi_q^{(2)}$, can be expressed as[3]

$$\chi_q^{(2)} \propto \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q} \tag{2S}$$

where ω_{IR} is the frequency of the incident IR beam. A_q, $\omega_q$and $2\Gamma_q$ are the amplitude, the frequency and the line-width (FWHM) of the vibrational transition. The amplitude, A_q, is non-zero only if both the Raman and infrared transitions are allowed. Hence, the resonant term dominates the intensity of the SFG signal when ω_{IR} is resonant with a surface vibrational mode that is both Raman and infrared active. Thus, neglecting cross terms and background contributions, the SFG relative intensity at the peak of the vibration resonance of two vibrational modes 1 and 2 is given by:

$$\frac{I_1}{I_2} = \left|\frac{A_1/\Gamma_1}{A_2/\Gamma_2}\right|^2$$

(3S).

SFG spectra are fitted with Eq. 1S to obtain all spectral parameters. Examples of best fits results to representative spectra on Au^{TS} and Au^{AD} surfaces for an odd and even number carbon alkanethiol are shown in Figures S1 and S2. The relative contributions of the different vibrational resonances to these spectra are shown with peak frequencies and relative intensities indicated. A summary of all the fitting parameters resulting from fitting the SFG spectra analyzed in this work are summarized in Table S1 and S2. NR and iNR are the real and imaginary components of the background term.

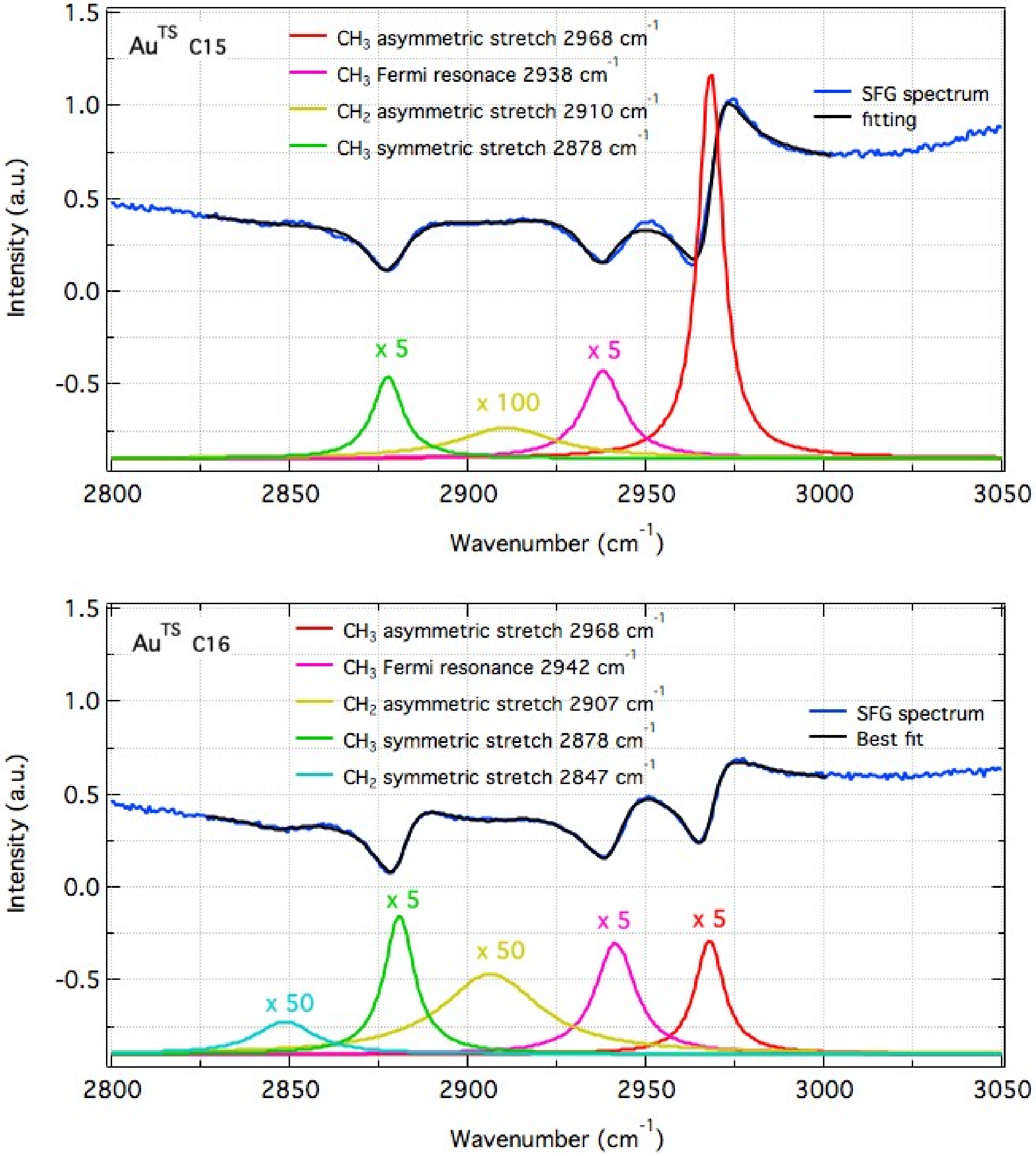

Figure S1. Fitting curves for SFG spectra of pentadecanethiolate (C_{15}) and hexadecanethiolate (C_{16}) SAMs fabricated on Au^{TS} surfaces.

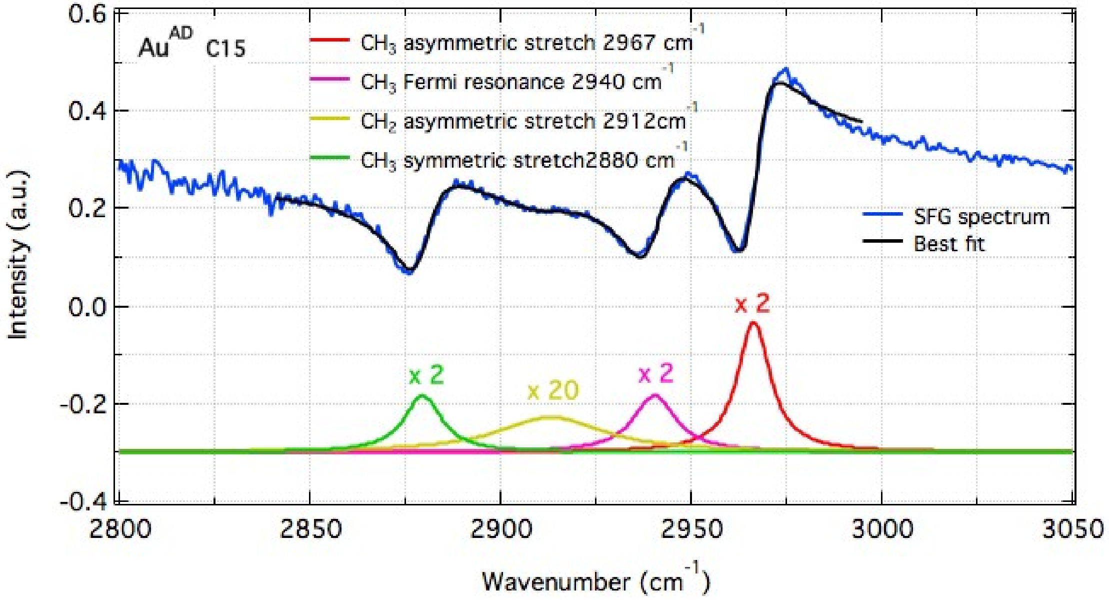

Figure S2. Fitting curves for SFG spectra of pentadecanethiolate (C_{15}) and hexadecanethiolate (C_{16}) SAMs fabricated on Au^{AD} surfaces.

Table S1. Fitting parameters of spectra derived from SAMs on Au^{TS}

Average value	**C9**	**C10**	**C11**	**C12**	**C14**	**C15**	**C16**
NR	0.18	0.35	0.15	0.41	0.37	0.13	0.40
iNR	0.74	0.62	0.74	0.57	0.59	0.79	0.57
A_1	5.61	1.67	6.30	1.85	1.66	6.73	1.62
ω_1	2968.52	2965.02	2966.78	2966.54	2965.59	2968.33	2967.66
Γ_1	4.12	4.79	4.54	5.29	4.86	4.66	4.65
A_2	2.11	2.36	2.01	2.40	2.34	2.05	2.33
ω_2	2938.88	2938.26	2936.15	2940.16	2939.15	2937.61	2941.16
Γ_2	6.80	6.80	6.80	6.80	6.80	6.80	6.80
A_3	1.35	1.22	0.99	1.50	1.23	1.01	1.40
ω_3	2908.39	2910.37	2906.19	2907.21	2907.29	2908.16	2907.85
Γ_3	16.90	16.90	16.90	16.90	16.90	16.90	16.90
A_4	1.82	2.24	1.80	2.18	2.14	1.77	2.14
ω_4	2878.91	2877.36	2876.37	2879.27	2878.22	2877.66	2880.49
Γ_4	5.80	5.80	5.80	5.80	5.80	5.80	5.80
A_5		0.62		0.65	0.56		0.58
ω_5		2845.37		2846.80	2846.26		2848.25
Γ_5		10.00		10.00	10.00		10.00
Standard deviation	C9	C10	C11	C12	C14	C15	C16
NR	0.04	0.01	0.01	0.02	0.02	0.01	0.02
iNR	0.0	0.00	0.01	0.02	0.00	0.01	0.01
A_1	0.42	0.07	0.05	0.06	0.07	0.20	0.09
ω_1	0.78	0.08	0.35	0.30	0.43	0.15	0.35
Γ_1	0.25	0.13	0.08	0.18	0.16	0.10	0.19
A_2	0.08	0.04	0.04	0.01	0.04	0.01	0.03
ω_2	0.49	0.12	0.18	0.30	0.51	0.04	0.44
Γ_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
A_3	0.31	0.07	0.04	0.06	0.11	0.01	0.17
ω_3	2.50	0.79	0.81	0.28	0.22	0.83	0.11
Γ_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
A_4	0.12	0.02	0.05	0.02	0.03	0.02	0.02
ω_4	0.24	0.08	0.15	0.31	0.54	0.00	0.40
Γ_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
A_5		0.04		0.00	0.03		0.08
ω_5		0.08		0.10	0.49		0.04
Γ_5		0.00		0.00	0.00		0.00

Table S2. Fitting parameters of spectra derived from SAMs on Au^{AD}

Average value	**C9**	**C10**	**C11**	**C12**	**C14**	**C15**	**C16**
NR	0.37	0.33	0.38	0.36	0.35	0.38	0.36
iNR	0.36	0.42	0.36	0.38	0.41	0.37	0.37
A_1	1.91	1.88	1.90	1.96	1.98	1.84	1.92
ω_1	2967.67	2966.59	2967.40	2967.15	2965.58	2966.35	2966.57
Γ_1	5.50	5.09	5.45	4.99	5.29	5.03	4.95
A_2	1.46	1.46	1.50	1.59	1.65	1.65	1.58
ω_2	2941.23	2939.88	2941.01	2940.82	2939.36	2940.42	2940.53
Γ_2	6.80	6.80	6.80	6.80	6.80	6.80	6.80
A_3	1.21	1.27	1.22	1.15	1.10	1.00	1.08
ω_3	2915.56	2915.72	2914.70	2913.83	2912.04	2912.06	2913.07
Γ_3	16.90	16.90	16.90	16.90	16.90	16.90	16.90
A_4	1.37	1.44	1.43	1.44	1.44	1.40	1.39
ω_4	2880.44	2878.94	2880.26	2879.91	2878.38	2879.52	2879.45
Γ_4	5.80	5.80	5.80	5.80	5.80	5.80	5.80
Standard deviation	C9	C10	C11	C12	C14	C15	C16
NR	0.02	0.00	0.01	0.01	0.01	0.02	0.01
iNR	0.01	0.01	0.00	0.01	0.01	0.00	0.01
A_1	0.02	0.02	0.01	0.10	0.11	0.00	0.06
ω_1	0.33	0.18	0.28	0.07	0.18	0.21	0.23
Γ_1	0.17	0.18	0.11	0.14	0.16	0.15	0.13
A_2	0.01	0.03	0.03	0.02	0.02	0.01	0.02
ω_2	0.06	0.11	0.29	0.18	0.01	0.10	0.13
Γ_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
A_3	0.01	0.05	0.04	0.06	0.11	0.05	0.03
ω_3	0.30	0.16	1.03	0.01	0.60	1.24	0.04
Γ_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
A_4	0.02	0.00	0.03	0.06	0.06	0.03	0.01
ω_4	0.31	0.08	0.28	0.11	0.17	0.16	0.25
Γ_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00

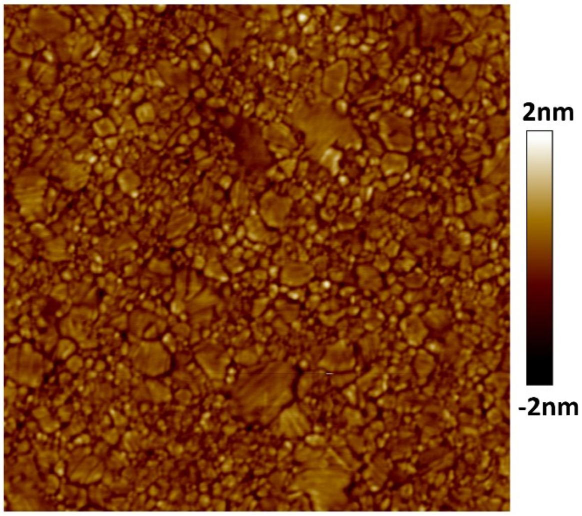

Figure S3. A zoomed-in AFM images of the Au^{TS} surface showing the grains and grain boundaries. Although these surfaces are not atomically flat, they have very small asperities and larger grain sizes.

Calculations for the dependence of SFG intensity on the tilting angle

The intensity of the sum frequency generation signal at ω_{SF} in the reflected or transmitted direction, $I(\omega_{SF})$, is given by

$$I(\omega_{SF}) \propto \left|\chi^{(2)}_{eff}\right|^2 I(\omega_{VIS}) I(\omega_{IR}) \tag{4S}$$

where $I(\omega_{VIS})$ and $I(\omega_{IR})$ are the intensities of the incident visible and IR laser beams, respectively. Here we will only be considering the SFG signal in the reflected direction.

The effective second order susceptibility, $\chi^{(2)}_{eff}$, defined further below, is proportional to the macroscopic susceptibility tensors, $\chi^{(2)}_{ijk}$, where *i*, *j*, and *k* correspond to the laboratory fixed frame. $\chi^{(2)}_{ijk}$ is related to the molecular hyperpolarizability $\beta^{(2)}_{i'j'k'}$ by

$$\chi^{(2)}_{ijk} = N_s \sum_{i'j'k'} \left\langle R_{ii'} R_{jj'} R_{kk'} \right\rangle \beta^{(2)}_{i'j'k'} \tag{5S}$$

where N_s is the vibrator number density at the interface and *i'*, *j'*, and *k'* could be *a*, *b*, or *c* in the molecular coordinate system. $R_{\lambda\lambda'}$ is the element of the Euler rotational transformation matrix that converts the molecular coordinate system $\lambda'(a,b,c)$ to the laboratory fixed frame $\lambda(x,y,z)$.

The SFG signal strength is thus strongly dependent on the number density and molecular orientation at the surface (Eqs. 4S and 5S). Since SFG signals are generated by the same alkanethiol molecules on both deposited and template-stripped gold surfaces, $\beta^{(2)}_{i'j'k'}$ is a constant when comparing the relative SFG intensities on these two surface types and thus, the main difference in the relative SFG signal strengths must be due to different orientations and/or different number of molecules on these surfaces.

For a rotationally isotropic interface ($C_{\infty v}$), the distinct polarization dependent $\chi_{eff}^{(2)}$ elements can be expressed in terms of specific experimental geometry configurations

$$\chi_{eff,ppp}^{(2)}$$

$$= -\ L_{xx}(\omega_{SF})L_{xx}(\omega_{VIS})L_{zz}(\omega_{IR})cos\varphi_{SF}cos\varphi_{VIS}sin\varphi_{IR}\chi_{xxz} - L_{xx}(\omega_{SF})L_{z}$$
$$cos\varphi_{SF}sin\varphi_{VIS}cos\varphi_{IR}\chi_{xzx} + L_{zz}(\omega_{SF})L_{xx}(\omega_{VIS})L_{xx}(\omega_{IR})sin\varphi_{SF}cos\varphi_{VIS}c$$
$$\chi_{zxx} + L_{zz}(\omega_{SF})L_{zz}(\omega_{VIS})L_{zz}(\omega_{IR})sin\varphi_{SF}sin\varphi_{VIS}sin\varphi_{IR}\chi_{zzz}$$

(6S)

where φ is the reflected angle of each beam with respect to the surface normal. In the laboratory coordinates $\lambda(x,y,z)$, all light beams propagate in the *xz* plane, which is perpendicular to the surface *xy* plane, with *z* as the surface normal direction. $L_{ii}(\omega)$ is the diagonal element of the Fresnel factor at frequency ω (where $\omega = \omega_{SF}, \omega_{VIS}\ or\ \omega_{IR}$) defined by,[1]

$$L_{xx}(\omega) = \frac{2n_1(\omega)cos\gamma}{n_1(\omega)cos\gamma + n_2(\omega)cos\varphi}$$

$$L_{yy}(\omega) = \frac{2n_1(\omega)cos\varphi}{n_1(\omega)cos\varphi + n_2(\omega)cos\gamma}$$

$$L_{zz}(\omega) = \frac{2n_2(\omega)cos\varphi}{n_1(\omega)cos\gamma + n_2(\omega)cos\varphi}\left(\frac{n_1(\omega)}{n^{'}(\omega)}\right)^2$$

(7S)

where $n_1(\omega), n_2(\omega),$ and $n^{'}(\omega)$ are the refractive index of first media (air), second media (liquid), and interfacial layer, respectively, at frequency ω and γ is the refracted angle for each beam.

Given the c_{3v} symmetry of the methyl group, there are 11 nonzero microscopic SFG hyperpolarizability elements for the methyl C-H vibrations.[33] With c along the c_3 axis of the methyl group, and the perpendicular *a* and *b* axes defined with the *a* axis along the projection of one C-H bond. For the symmetric stretching (ss) mode the non-zero hyperpolarizability elements are $\beta^{(2)}_{ccc}$ and $\beta^{(2)}_{aac} = \beta^{(2)}_{bbc}$, and correspondingly, for the asymmetric stretching (as) mode, the non-zero elements are $\beta^{(2)}_{aca} = \beta^{(2)}_{bcb}$, $\beta^{(2)}_{caa} = \beta^{(2)}_{cbb}$, and $\beta^{(2)}_{aaa} = -\beta^{(2)}_{bba} = -\beta^{(2)}_{abb} = -\beta^{(2)}_{bab}$. Thus, if θ is defined as the angle between the C$_3$ axis of methyl and the macroscopic surface normal, the $\chi^{(2)}_{ijk}$ elements are then given by,[2]

$$\chi^{(2),ss}_{xxz} = \chi^{(2),ss}_{yyz} = \frac{1}{2}N_s\beta^{(2)}_{ccc}[(1+R) < cos\theta > -(1-R) < cos^3\theta >]$$

$$\chi^{(2),ss}_{xzx} = \chi^{(2),ss}_{zxx} = \chi^{(2),ss}_{yzy} = \chi^{(2),ss}_{zyy} = \frac{1}{2}N_s\beta^{(2)}_{ccc}(1-R)[< cos\theta > - < cos^3\theta >]$$

$$\chi^{(2),ss}_{zzz} = N_s\beta^{(2)}_{ccc}[R < cos\theta > + (1-R) < cos^3\theta >]$$

$$\chi^{(2),as}_{xxz} = \chi^{(2),as}_{yyz} = -N_s\beta^{(2)}_{aca}(< cos\theta > - < cos^3\theta >)$$

$$\chi^{(2),as}_{xzx} = \chi^{(2),as}_{zxx} = \chi^{(2),as}_{yzy} = \chi^{(2),as}_{zyy} = N_s\beta^{(2)}_{aca} < cos^3\theta >$$

$$\chi^{(2),as}_{zzz} = 2N_s\beta^{(2)}_{aca}(< cos\theta > - < cos^3\theta >)$$

(8S)

where the ratio $R = \beta^{(2)}_{aac}/\beta^{(2)}_{ccc}$.

From the above expressions (Equations 4-8S) the ratio of the SFG intensity of the asymmetric/symmetric stretch bands on Au as a function of the tilting angle θ can be calculated (Supporting Information Figure S4) and is shown in Figure 4 for R= 1 and $\beta_{aca} / \beta_{ccc}$ = 1. (The exact values do not change the shape of the intensity ratio shown in Figure S4, just the absolute value of this quantity)

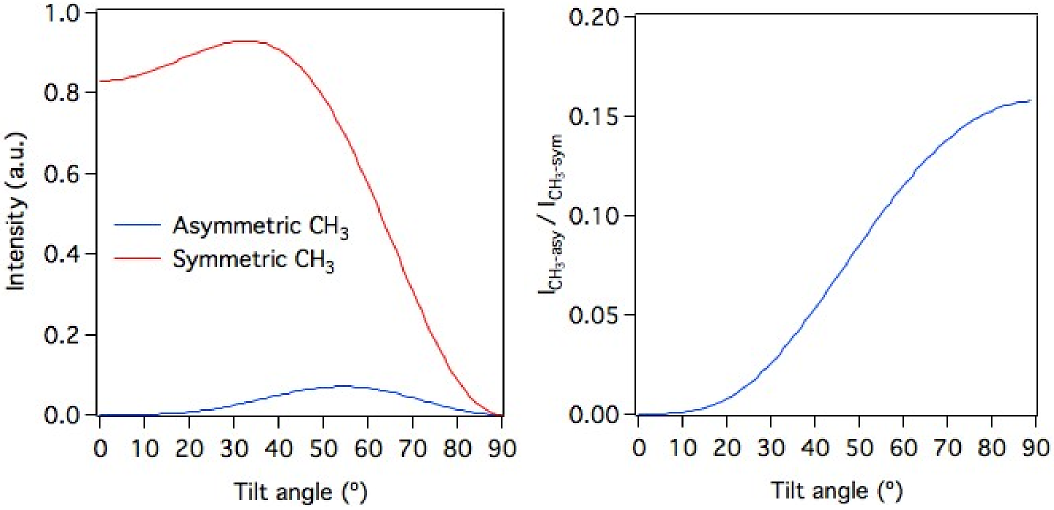

Figure S4. The dependence of SFG intensities of symmetric and asymmetric stretch of CH$_3$ on the tilt angle θ on gold surface.

Reference

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3. Wang, H.-F.,; Velarde, L.;Gan, W.; Fu, L., Quantitative Sum-Frequency Generation Vibrational Spectroscopy of Molecular Surfaces and Interfaces: Lineshape, Polarization, and Orientation. *Ann Rev Phys Chem* **2015**, 66,189