

Supporting Information:

Analysis of the interfacial molecular behavior of a lubrication film of n-dodecane containing stearic acid under lubricating conditions by sum frequency generation spectroscopy

(S-1) Measurement area

To confirm the measurement area of the TIR geometry, we performed SFG measurements under the static conditions and the static conditions with a silica spacer (Fig. S-1). Then, 100 μL of n-hexadecane was applied between the fused quartz prism and a sapphire disk. The distance between the prism and the disk in the static state with the spacer is 500 μm . The seeping distance of the evanescent light is less than 500 μm . Therefore, the interface between the prism and the n-hexadecane is detected in the case of the static state with a spacer. In both cases, the same SFG spectrum was observed. Therefore, even in the case of n-hexadecane, it is confirmed that the interface between the prism and n-hexadecane was detected, and the information from the interface between the n-hexadecane and the disk was not included.

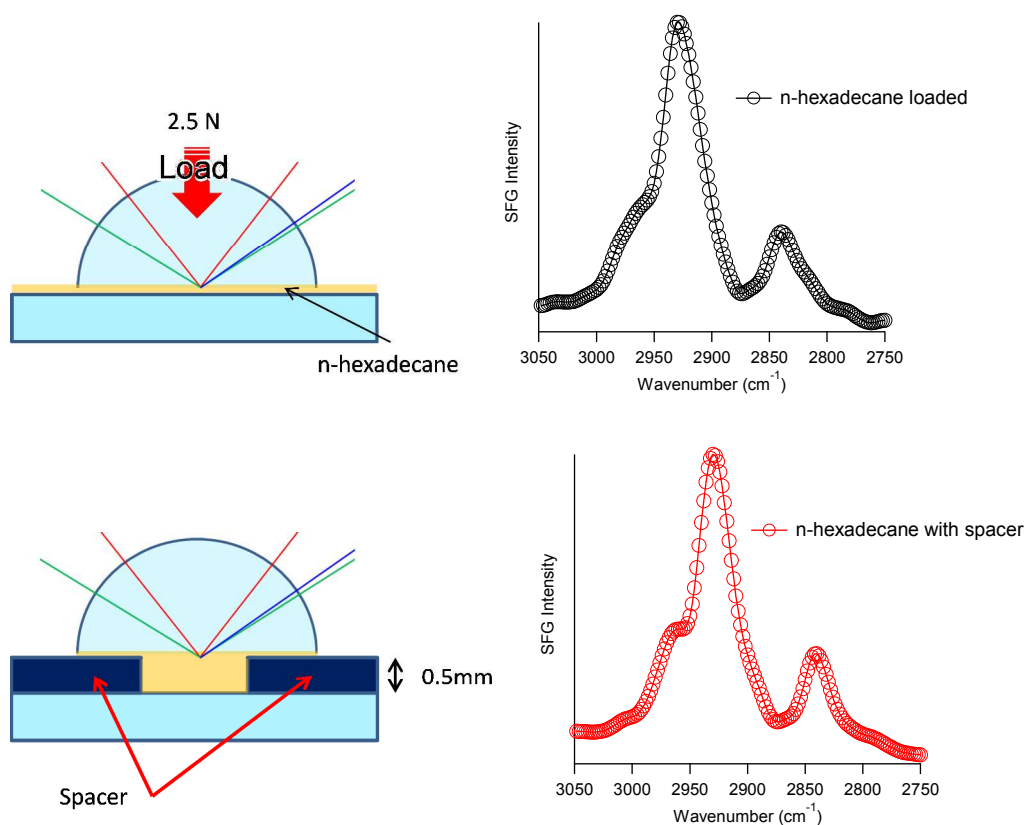


Fig. S-1. SFG spectra of n-hexadecane under the static conditions and the static conditions with a spacer

(S-2) Molecular orientation angle analysis

The experimental configuration from the interface is a square function of the effective sum frequency susceptibility $\chi_{eff}^{(2)}$.¹⁻⁵

$$I^{SFG}(\omega) = \frac{8\pi^3 \omega^2 \sec \beta^2}{c_0^3 n_1(\omega) n_1(\omega_1) n_1(\omega_2)} |\chi_{eff}^{(2)}|^2 I(\omega_1) I(\omega_2) \quad (1)$$

where ω , ω_1 , and ω_2 are the frequencies of the SFG, visible, and infrared beams, respectively; $n_i(\omega_i)$ is the refractive index in medium j ($j = 1, 2, \dots$) at frequency ω_i ; β is the reflection angle of SFG light; $I(\omega_1)$ and $I(\omega_2)$ are the intensities of visible and infrared incident light, respectively; and c_0 is the velocity of light in a vacuum. Here, $\chi_{eff}^{(2)}$ at the q -th resonant vibrational mode absorbance is¹⁻⁵

$$\chi_{eff}^{(2)} = \chi_{NR,eff}^{(2)} + \sum_q \frac{\chi_{q,eff}^{(2)}}{\omega_2 - \omega_q + i\Gamma_q} \quad (2)$$

where $\chi_{NR,eff}^{(2)}$ is the nonresonant contribution and $\chi_{q,eff}^{(2)}$ is the resonant susceptibility at the q -th resonant vibrational mode absorbance. $\chi_{q,eff}^{(2)}$ can be described as a function of the molecular orientation angles (θ , φ , χ) and the molecular hyperpolarizability $\beta_{q,ijk}$.

The effective nonlinear susceptibility $\chi_{q,eff}^{(2)}$ under *ppp* polarization is, according to,³⁻⁵

$$\begin{aligned} \chi_{q,eff}^{(2)PPP} = & -L_{xx}(\omega)L_{xx}(\omega_1)L_{zz}(\omega_2)\cos\beta\cos\beta_1\sin\beta_2\chi_{q,xxz} \\ & -L_{xx}(\omega)L_{zz}(\omega_1)L_{xx}(\omega_2)\cos\beta\sin\beta_1\cos\beta_2\chi_{q,xzx} \\ & +L_{zz}(\omega)L_{xx}(\omega_1)L_{xx}(\omega_2)\sin\beta\cos\beta_1\cos\beta_2\chi_{q,zxx} \\ & +L_{zz}(\omega)L_{zz}(\omega_1)L_{zz}(\omega_2)\sin\beta\sin\beta_1\sin\beta_2\chi_{q,zzz} \end{aligned} \quad (3)$$

where β , β_1 , and β_2 are the incident angles of SFG, visible, and infrared beams, respectively. The mode-specified $\chi_{q,ijk}$ tensors are related to the mode-specified molecular hyperpolarizability tensor in the molecular coordinate system $\lambda'(a, b, c)$ through the ensemble average over all of the possible molecular orientations. L_{xx} , L_{yy} , and L_{zz} are the Fresnel factors in the laboratory coordinate system $\lambda(x, y, z)$. Each Fresnel factor can be described as follows:^{3,6}

$$L_{xx} = \frac{2n_1 \cos \gamma}{n_1 \cos \gamma + n_2 \cos \beta} \quad (4a)$$

$$L_{yy} = \frac{2n_1 \cos \beta}{n_1 \cos \beta + n_2 \cos \gamma} \quad (4b)$$

$$L_{zz} = \frac{2n_2 \cos \beta}{n_1 \cos \gamma + n_2 \cos \beta} \left(\frac{n_1}{n'} \right)^2 \quad (4c)$$

where β is the incident angle and γ is the refraction angle. n_j is the refraction index at the interface, which was calculated using the method presented by Shen et al.³ We used the refractive indices of fused quartz of 1.419 for IR, 1.461 for VIS, and 1.467 for SFG.

The mode-specific $\chi_{q,ijk}$ tensors are considered. Each $\chi_{q,ijk}$ tensor of the symmetric stretching vibrational mode of C-H as a function of the tilt angle θ and the azimuthal angle χ is given by⁷

$$\begin{aligned} \chi_{xxz}^{(2)} = & \frac{1}{2} N_s (\beta_{aac} + \beta_{bbc}) \cos \theta \\ & - \frac{1}{4} N_s (\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (\cos \theta - \cos^3 \theta) (1 + \cos 2\chi) \end{aligned} \quad (5a)$$

$$\begin{aligned} \chi_{yyz}^{(2)} = & \frac{1}{2} N_s (\beta_{aac} + \beta_{bbc}) \cos \theta \\ & - \frac{1}{4} N_s (\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (\cos \theta - \cos^3 \theta) (1 - \cos 2\chi) \end{aligned} \quad (5b)$$

$$\begin{aligned} \chi_{xxz}^{(2)} = \chi_{zzx}^{(2)} = & \\ & - \frac{1}{4} N_s (\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) (\cos \theta + \cos^3 \theta) (1 + \cos 2\chi) \end{aligned} \quad (5c)$$

$$\begin{aligned} \chi_{zzz}^{(2)} = & \frac{1}{2} N_s (\beta_{aac} + \beta_{bbc}) \cos \theta \\ & - \frac{1}{2} N_s (\beta_{aac} + \beta_{bbc} - 2\beta_{ccc}) \cos^3 \theta \end{aligned} \quad (5d)$$

Each $\chi_{q,ijk}$ tensor of the antisymmetric stretching vibrational mode of C-H as a function of the tilt angle θ and the azimuthal angle χ is given by⁷

$$\chi_{xxz}^{(2)} = -\frac{1}{2} N_s \beta_{caa} (\cos \theta - \cos^3 \theta) (1 + \cos 2\chi) \quad (5a)$$

$$\chi_{yyz}^{(2)} = -\frac{1}{2} N_s \beta_{caa} (\cos \theta - \cos^3 \theta) (1 - \cos 2\chi) \quad (5b)$$

$$\begin{aligned} \chi_{xxz}^{(2)} = \chi_{zzx}^{(2)} = \\ \frac{1}{2} N_s \beta_{caa} [\cos \theta - (\cos \theta - \cos^3 \theta) (1 + \cos 2\chi)] \end{aligned} \quad (5c)$$

$$\chi_{zzz}^{(2)} = \beta_{caa} (\cos \theta - \cos^3 \theta) \quad (5d)$$

Each $\chi_{q,ijk}$ tensor of the symmetric stretching vibrational mode of C-H as a function of the tilt angle θ and the twist angle φ is given by^{1,7-9}

$$\begin{aligned} \chi_{xxz}^{(2)} = \chi_{yyz}^{(2)} = \frac{1}{2} N_s [\langle \cos^2 \varphi \rangle \beta_{aac} + \langle \sin^2 \varphi \rangle \beta_{bbc} + \beta_{ccc}] \cos \theta \\ + \frac{1}{2} N_s [\langle \sin^2 \varphi \rangle \beta_{aac} + \langle \cos^2 \varphi \rangle \beta_{bbc} - \beta_{ccc}] \cos^3 \theta \end{aligned} \quad (5a)$$

$$\begin{aligned} \chi_{xxz}^{(2)} = \chi_{zzx}^{(2)} = \chi_{yzy}^{(2)} = \chi_{zyy}^{(2)} = \\ -\frac{1}{2} N_s [\langle \sin^2 \varphi \rangle \beta_{aac} + \langle \cos^2 \varphi \rangle \beta_{bbc} - \beta_{ccc}] [\cos \theta - \langle \cos^3 \theta \rangle] \end{aligned} \quad (5b)$$

$$\begin{aligned} \chi_{zzz}^{(2)} = N_s [\langle \sin^2 \varphi \rangle \beta_{aac} + \langle \cos^2 \varphi \rangle \beta_{bbc}] \cos \theta \\ - N_s [\langle \sin^2 \varphi \rangle \beta_{aac} + \langle \cos^2 \varphi \rangle \beta_{bbc} - \beta_{ccc}] \cos^3 \theta \end{aligned} \quad (5c)$$

Each $\chi_{q,ijk}$ tensor of the antisymmetric stretching vibrational mode of C-H as a function of the tilt angle θ and the twist angle φ is given by^{1,7-9}

$$\chi_{xxz}^{(2)} = \chi_{yyz}^{(2)} = -N_s \beta_{aca} \langle \sin^2 \varphi \rangle [\cos \theta - \langle \cos^3 \theta \rangle] \quad (6a)$$

$$\begin{aligned} \chi_{xxz}^{(2)} = \chi_{zzx}^{(2)} = \chi_{yzy}^{(2)} = \chi_{zyy}^{(2)} = \\ \frac{1}{2} N_s \beta_{aca} [\langle \cos^2 \varphi \rangle - \langle \sin^2 \varphi \rangle] \cos \theta + N_s \beta_{aca} \langle \sin^2 \varphi \rangle \langle \cos^3 \theta \rangle \end{aligned} \quad (6b)$$

$$\chi_{zzz}^{(2)} = 2N_s \beta_{aca} \langle \sin^2 \varphi \rangle [\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle] \quad (6c)$$

The components of the transformation matrix depend on the Euler angles (θ, φ, χ) , which relate the molecular and laboratory fixed coordinate systems $\lambda(x, y, z)$. This $\chi_{q,eff}^{(2)}$ can be described as a function of the molecular orientation angle (θ, φ, χ) . A tilt angle θ of 0° is defined as the surface normal and that of 90° as parallel to the surface plane. A twist angle φ of 0° is defined as parallel to the surface and that of 90° as perpendicular to the surface. The azimuthal angle χ is within the plane of the surface. In this calculation, the average of the Euler angles can be determined for the rotationally isotropic system in the interface plane, that is, with no azimuthal angle χ dependence.

The tensor elements of $\beta_{q,ijk}$ are related to the IR and Raman properties of the q -th vibrational mode.^{5,7-9}

$$\beta_{q,i'j'k'}^{(2)} = -\frac{1}{2\varepsilon_0\omega_q} \frac{\partial \alpha_{i'j'}^{(1)}}{\partial Q_q} \frac{\partial \mu_{k'}}{\partial Q_q} \quad (7)$$

where $\partial \alpha_{q,ijk} / \partial Q_q$ and $\partial \mu_{q,ijk} / \partial Q_q$ are the partial derivatives of the Raman polarizability tensor and the IR dipole of the q -th vibrational mode, respectively. The hyperpolarizability tensors for the C-H stretching vibrational mode were determined by using the bond additive model outlined by Hirose et al. and Wang et al.^{8,10}

The relationship between the peak intensity ratio and the molecular orientation angle are shown in the manuscript on Fig. 4.

(S-3) Results of the curve fitting and molecular orientation angle

The SFG spectra of n-dodecane + SA under dynamic conditions are fitted by (eq.1) in the manuscript. The results are listed in Table S-1.

Table S-1 Fitting results of the SFG spectra of n-dodecane + SA during sliding

| n-dodecane + SA Rotation 0deg - ppp polarization | | | | |
|---|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| | CH ₂ v _{SS} | CH ₃ v _{SS} | CH ₂ v _{AS} | CH ₃ v _{AS} |
| ω_q (cm ⁻¹) | 2838 | 2893 | 2914 | 2964 |
| A_q (a.u.) | 9.74 | 4.43 | 6.56 | 2.45 |
| Γ_q (cm ⁻¹) | 13 | 12 | 17 | 11 |
| SFG-Intensity | 0.597 | 0.146 | 0.148 | 0.047 |
| Intensity ratio (CH ₂ -ss/CH ₂ -as) | | 4.04 | Tilt angle | 36.8° - 38.9° |
| n-dodecane + SA Rotation 20deg - ppp polarization | | | | |
| | CH ₂ v _{SS} | CH ₃ v _{SS} | CH ₂ v _{AS} | CH ₃ v _{AS} |
| ω_q (cm ⁻¹) | 2837 | 2887 | 2901 | |
| A_q (a.u.) | 8.29 | 2.52 | 3.84 | |
| Γ_q (cm ⁻¹) | 11 | 7 | 12 | |
| SFG-Intensity | 0.619 | 0.116 | 0.107 | |
| Intensity ratio (CH ₂ -ss/CH ₂ -as) | | 5.79 | Tilt angle | 33.3° - 35.1° |
| n-dodecane + SA Rotation 40deg - ppp polarization | | | | |
| | CH ₂ v _{SS} | CH ₃ v _{SS} | CH ₂ v _{AS} | CH ₃ v _{AS} |
| ω_q (cm ⁻¹) | 2794 | 2839 | 2890 | 2908 |
| A_q (a.u.) | 5.00 | 6.62 | 3.08 | 4.24 |
| Γ_q (cm ⁻¹) | 18 | 10 | 9 | 13 |
| SFG-Intensity | 0.082 | 0.460 | 0.122 | 0.110 |
| Intensity ratio (CH ₂ -ss/CH ₂ -as) | | 4.18 | Tilt angle | 36.5° - 38.5° |

| n-dodecane + SA Rotation 60deg - ppp polarization | | | | |
|---|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| | CH ₂ v _{SS} | CH ₃ v _{SS} | CH ₂ v _{AS} | CH ₃ v _{AS} |
| ω_q (cm ⁻¹) | 2838 | 2889 | 2907 | 2962 |
| A_q (a.u.) | 8.43 | 3.25 | 6.23 | 1.28 |
| Γ_q (cm ⁻¹) | 11 | 8 | 15 | 7 |
| SFG-Intensity | 0.562 | 0.147 | 0.162 | 0.034 |
| Intensity ratio (CH ₂ -ss/CH ₂ -as) | | 3.48 | Tilt angle | 38.4° - 40.6° |

| n-dodecane + SA Rotation 80deg - ppp polarization | | | | |
|---|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| | CH ₂ v _{SS} | CH ₃ v _{SS} | CH ₂ v _{AS} | CH ₃ v _{AS} |
| ω_q (cm ⁻¹) | 2836 | 2887 | 2900 | |
| A_q (a.u.) | 11.48 | 3.08 | 3.17 | |
| Γ_q (cm ⁻¹) | 13.47 | 7.41 | 8.77 | |
| SFG-Intensity | 0.726 | 0.173 | 0.130 | |
| Intensity ratio (CH ₂ -ss/CH ₂ -as) | | 5.57 | Tilt angle | 33.6° - 35.5° |

| n-dodecane + SA Rotation 80deg - ssp polarization | | | | |
|---|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| | CH ₂ v _{SS} | CH ₃ v _{SS} | CH ₂ v _{AS} | CH ₃ v _{AS} |
| ω_q (cm ⁻¹) | 2841 | | 2915 | 2941 |
| A_q (a.u.) | 10.12 | | 6.18 | 4.82 |
| Γ_q (cm ⁻¹) | 12 | | 15 | 13 |
| SFG-Intensity | 0.728 | | 0.159 | 0.146 |
| Intensity ratio (CH ₂ -ss/CH ₂ -as) | | 4.57 | Tilt angle | ~39.9° at 80° of χ |

(S-4) Sliding direction dependence of the SFG spectra of n-dodecane + stearic acid-d₃₅

To confirm that the strong CH₂-ss (symmetric stretching vibrational mode) peaks (in Fig. 2(b), Fig. 3(b) and Fig. 5) were derived from n-dodecane molecules, we used n-dodecane with stearic acid-d₃₅ as a lubricant. The static and dynamic SFG spectra of n-dodecane + SA-d₃₅ with ssp polarization are shown Fig. S-2 (a). In the case of the static condition, weak peaks at 2925 cm⁻¹ from CH₂-ss and 2960 cm⁻¹ from CH₃-as (asymmetric stretching vibrational mode) were observed. Under the dynamic conditions, a strong peak at 2840 cm⁻¹, which was attributed to CH₂-ss was observed. The sliding direction dependence of the SFG spectra of n-dodecane + SA-d₃₅ with ssp polarization is shown Fig. S-2 (b). Comparing Fig. S-2 (b) with Fig. 2 (b) in the manuscript, the same tendency regarding the CH₂ stretching vibrational mode was observed; a strong peak at 2840 cm⁻¹ was observed in all sliding directions. At a sliding direction of 80 deg, a peak at 2925 cm⁻¹, which was attributed to CH₂-as (antisymmetric stretching vibrational mode), was observed. Therefore, it is evident that the strong CH₂-ss peak (in Fig. 2(b), Fig. 3(b) and Fig. 5) was derived from the n-dodecane molecules.

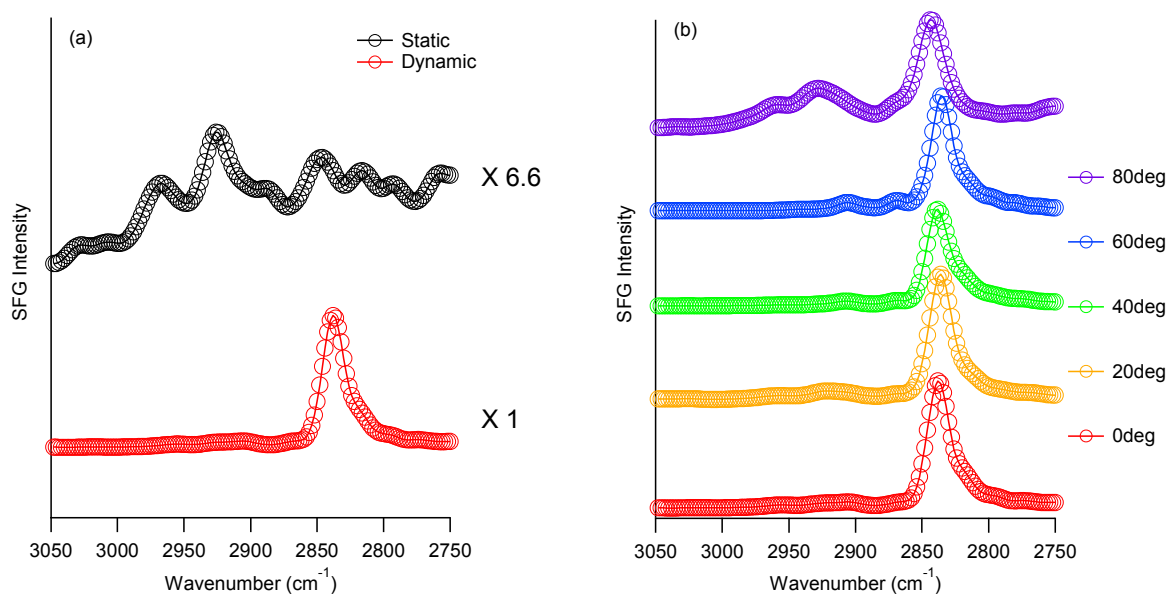


Fig. S-2. SFG spectra of n-dodecane + stearic acid-d₃₅ with ssp polarization in the wavenumber range of 2750 – 3050 cm⁻¹; (a) SFG spectra of static and dynamic condition, and (b) sliding direction dependence of SFG spectra.

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