

Vibrational Sum Frequency Generation Spectroscopy Measurement of the Rotational Barrier of Methyl Groups on Methyl-Terminated Silicon(111) Surfaces

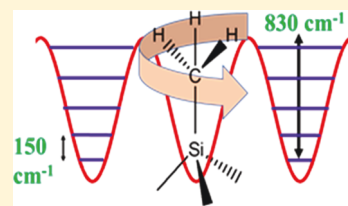
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Supporting Information

ABSTRACT: The methyl-terminated Si(111) surface possesses a 3-fold in-plane symmetry, with the methyl groups oriented perpendicular to the substrate. The propeller-like rotation of the methyl groups is hindered at room temperature and proceeds via 120° jumps between three isoenergetic minima in registry with the crystalline Si substrate. We have used line-shape analysis of polarization-selected vibrational sum frequency generation spectroscopy to determine the rotational relaxation rate of the surface methyl groups and have measured the temperature dependence of the relaxation rate between 20 and 120 °C. By fitting the measured rate to an Arrhenius dependence, we extracted an activation energy (the rotational barrier) of $830 \pm 360 \text{ cm}^{-1}$ and an attempt frequency of $(2.9 \pm 4.2) \times 10^{13} \text{ s}^{-1}$ for the methyl rotation process. Comparison with the harmonic frequency of a methyl group in a 3-fold cosine potential suggests that the hindered rotation occurs via uncorrelated jumps of single methyl groups rather than concerted gear-like rotation.



Functionalized Si(111) surfaces have important applications ranging from inorganic photovoltaics to nanoscale lithography.^{1–14} A monolayer of organic adsorbate covalently bonded to the surface Si atoms not only enhances the resistivity of the surface toward air oxidation^{15,16} but also allows tuning of the chemical reactivity at the surface.⁵ The methyl-terminated Si(111) surface is a singular example of such chemical functionalization, with all of the Si atoms at the topmost layer of the crystalline Si surface being covalently bonded to methyl groups through Si–C bonds. Previous theoretical^{17–19} and experimental studies^{20–24} have shown that these terminal methyl groups are oriented perpendicular to the Si substrate. Use of a two-step halogenation–methylation process via Grignard chemistry^{5,15,16} enables nearly 100% coverage of methyl groups on the atop Si atoms, resulting in a well-ordered, densely packed, chemically well-defined organic monolayer. Steric interactions between the adjacent methyl groups may hinder the rotation of –CH₃ groups along the Si–C bond, and therefore the orientation of the methyl groups might be interlocked at the interface.⁵

Several groups have studied the 3-fold azimuthal anisotropy of Si(111) surfaces by second harmonic generation (SHG) spectroscopy.^{25–27} SHG probes the electronic resonances of the Si substrate and therefore is not sensitive to the attached chemical groups. In contrast, vibrational sum frequency generation (VSFG) spectroscopy has provided information about the covalently attached functional groups on methyl-terminated²⁸ and propynyl-terminated Si(111) substrates.²⁹ Along with the 3-fold anisotropy of the Si(111) surface probed

by SHG spectroscopy, a 3-fold rotational anisotropy of covalently attached methyl and propynyl groups has been observed by VSFG spectroscopy, corroborating the proposition by Yamada et al.⁵ that the orientation of the methyl groups is interlocked at the interface because of steric interactions with the neighboring ligands. Line-shape analysis of VSFG spectra has also revealed that methyl groups on the methyl-terminated Si(111) surface undergo hindered rotation between the three isoenergetic equilibrium orientations at the interface.²⁸

In this work, we used surface-selective VSFG spectroscopy to investigate the energy barrier of the hindered rotation of methyl groups of the methyl-terminated Si(111) surface. Methyl-terminated Si(111) surfaces were prepared and characterized as described previously.^{30–32} To remove impurities, the samples were rinsed with water, acetone, methanol, and again with water and were heated in vacuo overnight at 450 °C. VSFG experiments before and after annealing the sample indicated that additional peaks associated with –CH₂ vibrational frequencies disappeared upon annealing and are thus consistently ascribed to impurities. A broadband femtosecond IR pulse centered around 3000 cm^{–1} with a fwhm of ~250 cm^{–1} was used to excite the symmetric and asymmetric stretching modes of the methyl groups. A narrowband picosecond 800 nm pulse upconverted the

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coherences, and the sum-frequency light was collected in the phase-matching direction. VSFG spectra were collected for two different polarization combinations of input and output beams: PPP and SPS, where the polarizations of the output SFG field and the input visible and IR fields are written from left to right. The sample was kept on top of a Peltier cooling–heating element that was glued over a water-cooled Al block, to allow measurement of VSFG spectra at five different temperatures between 20 and 120 °C. The sample chamber was continuously purged with dry air during the experiment. A thermocouple and an IR heat sensor were used to measure the temperature of the sample.

Infrared spectroscopy measurements of the methyl-terminated Si(111) samples showed characteristic peaks for the symmetric and asymmetric stretches of the methyl groups at 2910 and 2975 cm^{−1}, respectively.^{20,21} Figure 1 shows the

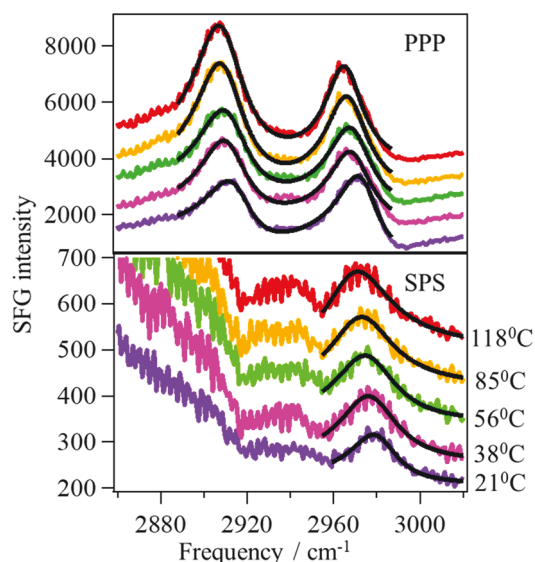


Figure 1. VSFG spectra of methyl-terminated Si(111) for PPP and SPS polarizations measured at five different temperatures. Spectra at different temperatures [blue (21 °C), purple (38 °C), green (56 °C), yellow (85 °C), and red (118 °C)] are stacked vertically, after adding a constant offset to each spectrum. In going from 21 to 118 °C, the offset values for PPP were −804, −400, 500, 1000, and 1500 and for SPS they were −50, −167, −50, 50, and 100. Black lines show spectral fitting as described in the text.

VSFG spectra for PPP and SPS polarizations. In the case of PPP polarization, two peaks were present, corresponding to the two IR-active modes of methyl groups; for SPS polarization, the peak corresponding to the symmetric stretching vibration was absent. The methyl groups are oriented perpendicular to the Si(111) substrate, so the transition dipole of the symmetric stretch (along its C_{3v} symmetry axis) is also perpendicular to the surface, whereas the transition dipole of the asymmetric stretch lies in the plane of the silicon substrate. As a result, S-polarized IR light, with the polarization in the plane of the substrate, cannot couple with the transition dipole of the symmetric stretch, but it can couple with the transition dipole of the asymmetric vibrational stretch. The large sloping response in the lower frequency side of the SPS spectra comes from the nonlinear nonresonant background in that region which could not be subtracted properly.

The effect of rotational dynamics on the lineshapes of the VSFG spectra has been described in detail by Vinaykin et al.³³ The basic assumption is that the vibrational dephasing is independent of the orientation of the molecule; hence, the second-order time-domain response function ($\chi^{(2)}(t)$) can be written as a multiplication of the vibrational dephasing term $V(t)$ and the rotational relaxation dynamics term $R(t)$ [$\chi^{(2)}(t) = V(t)R(t)$].³⁴ The vibrational dephasing was moreover assumed to be exponential; i.e., $V(t) \propto e^{-\Gamma_v t} \cos(\omega_0 t)$, where Γ_v is the damping constant. A general theoretical framework was presented to calculate the orientational part of the response function $R(t)$ within the small-angle rotational diffusion approximation.^{35–37} In the weak-confinement model, the orienting potential is assumed to be on the order of $k_B T$ (where k_B is Boltzmann's constant) and the rotational diffusion in the surface is approximated by free anisotropic diffusion with different relaxation rates in-plane ($D_{||}$) and out-of-plane ($D_{\perp}$).³⁸ For the methyl-terminated Si surface, the methyl groups rotate with respect to the C_{3v} symmetry axis perpendicular to the surface plane; hence, there is zero out-of-plane diffusion, i.e. $D_{\perp} = 0$. In this case, the SFG response function calculated by Vinaykin et al.³³ can be rewritten as

$$\chi_{\text{PPP}}^{(2)}(t) = (C_1^{\text{PPP}} + C_3^{\text{PPP}} e^{-D_{||} t}) e^{-\Gamma_v t} \cos(\omega_0 t) \quad (1)$$

$$\chi_{\text{SPS}}^{(2)}(t) = C_3^{\text{SPS}} e^{-D_{||} t} e^{-\Gamma_v t} \cos(\omega_0 t) \quad (2)$$

where the term C_1^{PPP} represents pure vibrational dephasing, and the other two terms (C_3^{PPP} and C_3^{SPS}) have contributions from both rotational and vibrational relaxations. For a molecule oriented vertically to an azimuthally isotropic surface (tilt angle $\approx 0^\circ$ from the surface normal) and undergoing rotational diffusion about an axis perpendicular to the surface plane, the PPP line-shape is dominated by the vibrational dephasing term (C_1^{PPP}) and is insensitive to the reorientational dynamics on the same time scale ($C_3^{\text{PPP}} = 0$).³³ The modified response function for PPP polarization is thus

$$\chi_{\text{PPP}}^{(2)}(t) = C_1^{\text{PPP}} e^{-\Gamma_v t} \cos(\omega_0 t) \quad (3)$$

In contrast with the small-angle rotational diffusion approximation, the rotational relaxation on the $\text{CH}_3\text{-Si(111)}$ surface presumably occurs via 120° jumps of the methyl groups between three isoenergetic conformations and cannot be considered per se as a small-step diffusion. Hence, assuming first-order decay kinetics, the response functions (eqs 1–3) are the same, with the in-plane diffusion constant ($D_{||}$) replaced by the rate constant (k_{rot}) of such hindered rotation.

The frequency domain response functions are obtained by Fourier transforming eqs 2 and 3, and the line-shapes are Lorentzian:

$$\chi_{\text{SPS}}^{(2)}(\omega) = \frac{A_{\text{SPS}}}{(\omega - \omega_0) + i\Gamma_{\text{SPS}}} \quad \text{where } \Gamma_{\text{SPS}} = \Gamma_v + k_{\text{rot}} \quad (4)$$

$$\chi_{\text{PPP}}^{(2)}(\omega) = \frac{A_{\text{PPP}}}{(\omega - \omega_0) + i\Gamma_{\text{PPP}}} \quad \text{where } \Gamma_{\text{PPP}} = \Gamma_v \quad (5)$$

where A is the amplitude and Γ is the HWHM of the Lorentzian. The line width of the SPS spectra has contributions from both the vibrational dephasing and in-plane orientation dynamics, whereas the PPP line width has only a vibrational dephasing contribution. For methyl-terminated Si(111), the $-\text{CH}_3$ groups are oriented perpen-

dicular to the substrate, and the transition dipole of the asymmetric stretch lies parallel to the surface plane. Rotation of the methyl groups along the C_{3v} symmetry axis results in the in-plane rotation of the asymmetric stretch transition dipole, which manifests itself as a line broadening in the SPS spectra. The line width of the PPP spectra, however, is not affected by such rotation. The difference between SPS and PPP line width for the asymmetric stretch vibration contains information about the reorientation dynamics of the molecule.^{33,39}

$$\Gamma_{\text{SPS}} - \Gamma_{\text{PPP}} = k_{\text{rot}} \quad (6)$$

Figure 1 also shows the SFG spectra of the $\text{H}_3\text{C-Si(111)}$ surface measured at five different temperatures. The SFG spectra were fitted using the following equation:⁴⁰

$$I_{\text{SFG}}(\omega) = \left| A_{\text{NR}} e^{i\varphi} + \sum_{j=1}^n \frac{B_j}{\omega - \omega_j + i\Gamma_j} \right|^2 \quad (7)$$

where A_{NR} and φ are the amplitude and phase, respectively, of the nonresonant background relative to the resonant contribution. The resonant part for the j th vibrational mode is expressed as a Lorentzian with an amplitude of B_j/Γ_j , a center frequency ω_j , and a line-width Γ_j . Each PPP spectrum was fitted with two Lorentzians (for the symmetric and asymmetric stretch modes), and one Lorentzian (asymmetric stretch) was used to fit the SPS spectra. For the asymmetric stretch mode, the change in Γ_{PPP} and Γ_{SPS} with temperature is shown in Figure 2. Γ_{SPS} exhibited a monotonic increase with

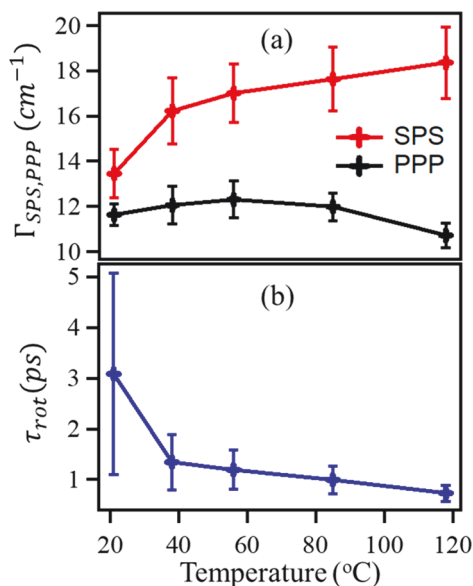


Figure 2. Plot of (a) PPP and SPS line widths of the asymmetric $-\text{CH}_3$ stretch frequency vs temperature; (b) rotational relaxation time scale vs temperature.

increasing temperature, whereas Γ_{PPP} did not show a substantial change between 20 and 90 $^{\circ}\text{C}$ with, however, a noticeable decrease in line width above 90 $^{\circ}\text{C}$. Because the methyl groups in the methyl-terminated Si(111) sample have a rotational barrier,²⁸ an increase in temperature populates higher rotational levels of the molecule and leads to faster rotation. As a result, rotational relaxation becomes more rapid with increase in temperature, giving rise to the increase in SPS line width. The PPP spectrum, however, is not affected by the

reorientation dynamics; hence, Γ_{PPP} is almost constant within the temperature range explored in our work. The slight decrease observed in the PPP line width at higher temperature could be due to motional narrowing.^{41,42}

Following eq 6, k_{rot} (cm^{-1}) can be calculated at every temperature, and assuming the Lorentzian spectral line shape, the time scale of rotational relaxation (τ_{rot}) is obtained by the equation $\tau_{\text{rot}} = 1/2\pi ck_{\text{rot}}$ where c is the speed of light. At 21 $^{\circ}\text{C}$, the rotational relaxation time scale is 3 ± 2 ps, whereas, at 118 $^{\circ}\text{C}$, τ_{rot} is 730 ± 160 fs. The measurements are consistent with the room-temperature rotational dephasing of methyl groups for methyl-terminated Si(111) reported by Malyk et al.,²⁸ in which $k_{\text{rot}} = 3.5 \pm 1.5 \text{ cm}^{-1}$, indicating a rotational time scale of $\tau_{\text{rot}} = 1\text{--}2$ ps. Use of a classical correlation function⁴³ for the free-rotors predicts that the time scale of rotational dephasing for a free methyl rotor is ~ 100 fs at room temperature. The rotational barrier in methyl-terminated Si(111) thus decreases the methyl rotation by more than an order of magnitude relative to a free rotor.

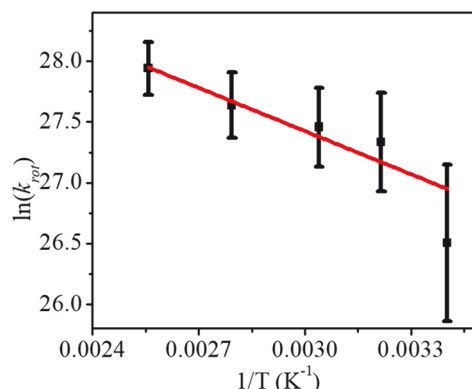


Figure 3. Plot of $\ln(k_{\text{rot}})$ vs $1/T$, where k_{rot} is the rotational rate constant, and T is the temperature in Kelvin. The plot is fitted with a straight line (red). The slope and the intercept of the fitted line are used to calculate the rotational barrier (E_{rot}) and the attempt frequency (k_0).

Figure 3 shows the natural logarithm of the rate constant, $\ln(k_{\text{rot}})$, plotted against $1/T$ according to the Arrhenius equation

$$\ln(k_{\text{rot}}) = \ln(k_0) - \frac{E_{\text{rot}}}{R} \frac{1}{T} \quad (8)$$

where T is the temperature in Kelvin; E_{rot} is the activation energy, which in our case is the barrier of methyl rotation; k_0 is the attempt frequency. The activation barrier of the methyl rotation was calculated from the slope of the fitted straight line, $-\frac{E_{\text{rot}}}{R}$, yielding a value of $E_{\text{rot}} = 2.4 \pm 1.0$ kcal/mol, which is equivalent to 9.9 ± 4.3 kJ/mol, or $830 \pm 360 \text{ cm}^{-1}$. Using density functional perturbation theory, Brown et al.⁴⁴ calculated the upper bound of the rotational barrier of methyl groups on a methyl terminated Si(111) surface. On a fully methylated surface, a single methyl group was rotated while holding the neighboring methyl groups fixed, not allowing them to undergo any kind of correlated motion to minimize the steric interactions. The theoretically calculated upper bound, i.e., $112 \text{ meV} \approx 900 \text{ cm}^{-1}$, is in excellent agreement with our experimentally determined rotational barrier. The

methyl internal rotational barrier in some common organic compounds ranges from 10 cm⁻¹ (toluene)^{45,46} to 514 cm⁻¹ (³⁵Cl-*o*-chlorotoluene)⁴⁷ to ~1000 cm⁻¹ (ethane)⁴⁸ (Table 1). The attempt frequency (k_0) can be calculated from the

Table 1. Torsional Barrier of Methyl Groups in Different Organic Compounds Tabulated from the Literature

compound	methyl rotational barrier (cm ⁻¹)
toluene	10 ^{45,46}
<i>o</i> -fluorotoluene	227 ⁴⁹
³⁵ Cl- <i>o</i> -chlorotoluene	514 ⁴⁷
³⁷ Cl- <i>o</i> -chlorotoluene	507 ⁴⁷
<i>o</i> -methylanisole	444 ⁵⁰
<i>o</i> -xylene	518 ⁵¹
acetaldehyde	408 ^{52–55}
anti- <i>o</i> -cresol	370 ⁵⁶
syn- <i>o</i> -cresol	661 ⁵⁶
methylsilane	500 ⁴⁴
ethane	1100 ⁴⁸

intercept, $\ln(k_0)$, and is estimated to be $2.9 \times 10^{13} \text{ s}^{-1}$ (i.e., 29 ps⁻¹ or $2.9 \times 10^{-2} \text{ fs}^{-1}$) for CH₃-Si(111), which corresponds to a frequency of 150 cm⁻¹ for the restricted rotation.

As mentioned above, three preferential orientations of the methyl groups are present on the methyl-terminated Si(111) surface, and the methyl groups switch between these three isoenergetic conformations by hindered rotation along the torsional vibrational coordinate with respect to the C–Si bond. A simple mathematical function that gives the correct 3-fold symmetric potential can be written in the form $V(\varphi) = \frac{1}{2}E_{\text{rot}}(1 - \cos(3\varphi))$,⁴³ where φ is the torsional angle and E_{rot} is the barrier of rotation. Solving the Schrodinger equation for this potential and assuming that the thermal energy is smaller than the rotational barrier, i.e. $k_{\text{B}}T \ll E_{\text{rot}}$, yields an expression for the harmonic frequency (ν) of the torsional motion as⁴³

$$\nu = \frac{3}{2\pi} \left(\frac{E_{\text{rot}}}{2I_r} \right)^{1/2} \quad (9)$$

where I_r is the reduced moment of inertia of a single methyl group with respect to the axis along the C–Si bond. Using $I_r = 3.260 \text{ amu } \text{\AA}^2$ and $E_{\text{rot}} = 9.9 \text{ kJ/mol}$, the frequency of torsional motion is calculated to be 190 cm⁻¹. This calculated torsional frequency for a single methyl group matches well with the experimentally determined attempt frequency (150 cm⁻¹) of the methyl-terminated Si(111) sample. This agreement suggests that the rotation of the methyl groups is independent from each other, as opposed to a gear-like concerted rotation of multiple methyl groups on the surface. Thus, at room temperature, the rotational relaxation of a single methyl group thus seems to occur without any correlation with the adjacent methyl moieties. As a potential subject for future studies, it is interesting to speculate whether a different mechanism, such as gear-like concerted rotation of multiple methyl groups, can become important at lower temperatures.

A similar experiment can be done for the CD₃-Si(111) system. Brown et al.⁴⁴ reported the frequency of the hindered methyl rotation to be 29.0 meV $\approx$ 234 cm⁻¹ for CH₃-Si(111) and 20.8 meV $\approx$ 168 cm⁻¹ for CD₃-Si(111) at the $\bar{\Gamma}$ -point. Deuteration of the methyl groups thus results in decreasing the attempt frequency of the rotational motion by a factor of

$(\sqrt{2})^{-1}$ and also lowers the zero-point energy along the torsional vibrational coordinate. As a consequence, the rotational activation barrier of the methyl groups for a CD₃-Si(111) system will be higher as compared to that of the CH₃-Si(111) system. It is worth noting that resonant vibrational energy transfer can happen via coupling of the transition dipoles between neighboring methyl groups, and it is one of the possible mechanisms for orientational dephasing in methyl-terminated silicon(111) surfaces. Isotopic dilution of the CH₃-Si(111) substrate effectively gives us a tool to tune such dipole–dipole coupling, which directly influences the vibrational and rotational dephasing. Therefore, using a mixed layer of CH₃- and CD₃-terminated Si(111) surface or a highly diluted CH₃-Si(111) surface will be a classic way to decouple different dephasing channels. One practical problem will be to record the SPS spectra for the isotopically diluted samples because of its considerably low signal-to-noise ratio.

We have used VSFG spectroscopy to determine the rotational barrier of methyl groups of the methyl-terminated silicon(111) surface. The methyl groups are oriented perpendicular to the Si substrate and cannot rotate freely because of steric interactions with the adjacent methyl moieties. As a result, the VSFG response from the C–H stretches of the methyl groups showed a 3-fold rotational anisotropy. The room-temperature PPP versus SPS line-shape analysis predicts a possibility of hindered rotation of the methyl groups between three isoenergetic equilibrium configurations. For a “rod-like molecule” standing perpendicular to the substrate and rotating with respect to the surface normal, the PPP spectral line-shape is mainly dominated by the vibrational relaxation, whereas the SPS spectrum carries information about both the vibrational dephasing and rotational dynamics. Increasing temperature results in faster rotational relaxation, which manifests itself in the increase in SPS line width. Therefore, the difference between SPS and PPP line width increases with temperature and measures the contribution of the reorientation dynamics in the VSFG spectra for the CH₃-Si(111) surface. Fitting the rate constant of rotational relaxation (k_{rot}) to the Arrhenius equation yields the energy barrier of rotation, $E_{\text{rot}} = 830 \pm 360 \text{ cm}^{-1}$, as well as the attempt frequency, $k_0 = 2.9 \times 10^{13} \text{ s}^{-1}$. The experimentally determined attempt frequency matches well with the calculated harmonic torsional frequency of a single methyl group. This accord suggests that the methyl rotation on the CH₃-Si(111) surface is not a concerted gear-like motion involving multiple methyl groups but rather represents the rotation of an individual methyl group uncorrelated from the rest of the surface functionality. This work thus demonstrates a unique application of VSFG spectral line-shape analysis to visualize the mechanistic details of a hindered methyl rotation on a methyl-terminated Si(111) surface.

EXPERIMENTAL METHODS

A dual-stage Ti:Sapphire amplifier system operating at a 5 kHz repetition rate and generating a femtosecond 800 nm pulse with a pulse energy of 3 mJ was used to generate the light pulses for VSFG spectroscopy. One portion of the amplifier output (pulse width of $\sim 40 \text{ fs}$ and pulse energy of 1.5 mJ) was used to pump the TOPAS optical parametric amplifier (OPA). The outputs from the OPA (signal and idler) were routed to the noncollinear difference frequency generator (NDFG) to generate a broadband mid-infrared pulse centered around 3000

cm^{-1} with a bandwidth of 250 cm^{-1} . The other portion of the amplifier output was first externally compressed using a grating compressor and then passed through a 4f stretcher to narrow the pulse in frequency domain and produce a boxcar spectral profile. The frequency resolution was achieved by this picosecond 800 nm up-conversion pulse ($\text{fwhm} \approx 8\text{--}10\text{ cm}^{-1}$). At the sample, the power of the IR light was $4\text{ }\mu\text{J/pulse}$ and that of the visible light was $7\text{ }\mu\text{J/pulse}$. The spot-size of the IR and the visible beams were 190 and $230\text{ }\mu\text{m}$, respectively. The angle of incidence of the visible and the IR beam was 67° and 62° with respect to the surface normal, respectively. The SFG spectra were recorded using a liquid-nitrogen-cooled CCD detector (2048×512 pixels). To perform temperature-dependent experiments, a commercial Peltier cooler (MARLOW Industries, model no RC12-8L) was purchased and glued over a hollow Al block through which room-temperature water was flowed by an external pump. The sample was kept on top of that Peltier cooling/heating element. A voltage versus temperature calibration plot was created by changing the input voltage of the Peltier cooler and measuring the temperature of the sample using a thermocouple as well as an IR heat sensor. The sample chamber was continuously purged with dry air during the experiment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpcl.9b01487](https://doi.org/10.1021/acs.jpcl.9b01487).

Experimental details and spectral fitting parameters of SFG data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Yates, J. T. A new opportunity in silicon-based microelectronics. *Science* **1998**, *279* (5349), 335–336.
- (2) Ashkenasy, G.; Cahen, D.; Cohen, R.; Shanzer, A.; Vilan, A. Molecular engineering of semiconductor surfaces and devices. *Acc. Chem. Res.* **2002**, *35* (2), 121–128.
- (3) Wong, K. T.; Lewis, N. S. What a difference a bond makes: the structural, chemical, and physical properties of methyl-terminated Si (111) surfaces. *Acc. Chem. Res.* **2014**, *47* (10), 3037–3044.
- (4) Shen, X.; Sun, B.; Yan, F.; Zhao, J.; Zhang, F.; Wang, S.; Zhu, X.; Lee, S. High-performance photoelectrochemical cells from ionic liquid

electrolyte in methyl-terminated silicon nanowire arrays. *ACS Nano* **2010**, *4* (10), 5869–5876.

(5) Yamada, T.; Kawai, M.; Wawro, A.; Suto, S.; Kasuya, A. HREELS, STM, and STS study of CH₃-terminated Si (111)-(1 $\times$ 1) surface. *J. Chem. Phys.* **2004**, *121* (21), 10660–10667.

(6) Haick, H.; Hurley, P. T.; Hochbaum, A. I.; Yang, P.; Lewis, N. S. Electrical characteristics and chemical stability of non-oxidized, methyl-terminated silicon nanowires. *J. Am. Chem. Soc.* **2006**, *128* (28), 8990–8991.

(7) Punireddi, S. R.; Assad, O.; Haick, H. Highly stable organic monolayers for reacting silicon with further functionalities: the effect of the C–C Bond nearest the silicon surface. *J. Am. Chem. Soc.* **2008**, *130* (41), 13727–13734.

(8) Vilan, A.; Yaffe, O.; Biller, A.; Salomon, A.; Kahn, A.; Cahen, D. Molecules on Si: electronics with chemistry. *Adv. Mater.* **2010**, *22* (2), 140–159.

(9) Filler, M. A.; Bent, S. F. The surface as molecular reagent: organic chemistry at the semiconductor interface. *Prog. Surf. Sci.* **2003**, *73* (1–3), 1–56.

(10) Seitz, O.; Vilan, A.; Cohen, H.; Hwang, J.; Haeming, M.; Schoell, A.; Umbach, E.; Kahn, A.; Cahen, D. Doping molecular monolayers: effects on electrical transport through alkyl chains on silicon. *Adv. Funct. Mater.* **2008**, *18* (14), 2102–2113.

(11) Li, Y.; O'Leary, L. E.; Lewis, N. S.; Galli, G. Combined theoretical and experimental study of band-edge control of Si through surface functionalization. *J. Phys. Chem. C* **2013**, *117* (10), 5188–5194.

(12) Touahir, L.; Allongue, P.; Aureau, D.; Boukherroub, R.; Chazalviel, J.-N.; Galopin, E.; Gouget-Laemmel, A.; de Villeneuve, C. H.; Morailon, A.; Niedziółka-Jönsson, J.; et al. Molecular monolayers on silicon as substrates for biosensors. *Bioelectrochemistry* **2010**, *80* (1), 17–25.

(13) Maldonado, S.; Plass, K. E.; Knapp, D.; Lewis, N. S. Electrical properties of junctions between Hg and Si (111) surfaces functionalized with short-chain alkyls. *J. Phys. Chem. C* **2007**, *111* (48), 17690–17699.

(14) Loscutoff, P. W.; Bent, S. F. Reactivity of the germanium surface: chemical passivation and functionalization. *Annu. Rev. Phys. Chem.* **2006**, *57*, 467–495.

(15) Webb, L. J.; Lewis, N. S. Comparison of the electrical properties and chemical stability of crystalline silicon (111) surfaces alkylated using grignard reagents or olefins with Lewis acid catalysts. *J. Phys. Chem. B* **2003**, *107* (23), 5404–5412.

(16) Royea, W. J.; Juang, A.; Lewis, N. S. Preparation of air-stable, low recombination velocity Si (111) surfaces through alkyl termination. *Appl. Phys. Lett.* **2000**, *77* (13), 1988–1990.

(17) Ferguson, G. A.; Raghavachari, K. The emergence of collective vibrations in cluster models: Quantum chemical study of the methyl-terminated Si (111) surface. *J. Chem. Phys.* **2006**, *125* (15), 154708.

(18) Solares, S. D.; Yu, H.; Webb, L. J.; Lewis, N. S.; Heath, J. R.; Goddard, W. A. Chlorination- Methylation of the Hydrogen-Terminated Silicon (111) Surface Can Induce a Stacking Fault in the Presence of Etch Pits. *J. Am. Chem. Soc.* **2006**, *128* (12), 3850–3851.

(19) Aliano, A.; Li, Y.; Cicero, G.; Galli, G. Structural and electronic properties of the methyl-terminated si (111) surface. *J. Phys. Chem. C* **2010**, *114* (27), 11898–11902.

(20) Johansson, E.; Hurley, P. T.; Brunschwig, B. S.; Lewis, N. S. Infrared vibrational spectroscopy of isotopically labeled ethyl-terminated si (111) surfaces prepared using a two-step chlorination/alkylation procedure. *J. Phys. Chem. C* **2009**, *113* (34), 15239–15245.

(21) Webb, L. J.; Rivillon, S.; Michalak, D. J.; Chabal, Y. J.; Lewis, N. S. Transmission infrared spectroscopy of methyl- and ethyl-terminated silicon (111) surfaces. *J. Phys. Chem. B* **2006**, *110* (14), 7349–7356.

(22) Yu, H.; Webb, L. J.; Heath, J. R.; Lewis, N. S. Scanning tunneling spectroscopy of methyl- and ethyl-terminated Si (111) surfaces. *Appl. Phys. Lett.* **2006**, *88* (25), 252111.

- (23) Yu, H.; Webb, L. J.; Ries, R. S.; Solares, S. D.; Goddard, W. A.; Heath, J. R.; Lewis, N. S. Low-temperature STM images of methyl-terminated Si (111) surfaces. *J. Phys. Chem. B* **2005**, *109* (2), 671–674.
- (24) Becker, J. S.; Brown, R. D.; Johansson, E.; Lewis, N. S.; Sibener, S. Helium atom diffraction measurements of the surface structure and vibrational dynamics of CH 3–Si (111) and CD 3–Si (111) surfaces. *J. Chem. Phys.* **2010**, *133* (10), 104705.
- (25) Tom, H.; Heinz, T.; Shen, Y. Second-harmonic reflection from silicon surfaces and its relation to structural symmetry. *Phys. Rev. Lett.* **1983**, *51* (21), 1983.
- (26) Sipe, J.; Moss, D.; Van Driel, H. Phenomenological theory of optical second-and third-harmonic generation from cubic centrosymmetric crystals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1987**, *35* (3), 1129.
- (27) Mitchell, S.; Boukherroub, R.; Anderson, S. Second harmonic generation at chemically modified Si (111) surfaces. *J. Phys. Chem. B* **2000**, *104* (32), 7668–7676.
- (28) Malyk, S.; Shalhout, F. Y.; O'Leary, L. E.; Lewis, N. S.; Benderskii, A. V. Vibrational sum frequency spectroscopic investigation of the azimuthal anisotropy and rotational dynamics of methyl-terminated silicon (111) surfaces. *J. Phys. Chem. C* **2013**, *117* (2), 935–944.
- (29) Dhar, P.; Plymale, N. T.; Malyk, S.; Lewis, N. S.; Benderskii, A. V. Vibrational Sum-Frequency Spectroscopic Investigation of the Structure and Azimuthal Anisotropy of Propynyl-Terminated Si (111) Surfaces. *J. Phys. Chem. C* **2017**, *121* (31), 16872–16878.
- (30) Bansal, A.; Li, X.; Lauermaun, I.; Lewis, N. S.; Yi, S. I.; Weinberg, W. Alkylation of Si surfaces using a two-step halogenation/Grignard route. *J. Am. Chem. Soc.* **1996**, *118* (30), 7225–7226.
- (31) Bansal, A.; Li, X.; Yi, S. I.; Weinberg, W.; Lewis, N. S. Spectroscopic studies of the modification of crystalline Si (111) surfaces with covalently-attached alkyl chains using a chlorination/alkylation method. *J. Phys. Chem. B* **2001**, *105* (42), 10266–10277.
- (32) O'Leary, L. E.; Johansson, E.; Brunschwig, B. S.; Lewis, N. S. Synthesis and characterization of mixed methyl/allyl monolayers on Si (111). *J. Phys. Chem. B* **2010**, *114* (45), 14298–14302.
- (33) Vinaykin, M.; Benderskii, A. V. Orientational Dynamics in Sum Frequency Spectroscopic Line Shapes. *J. Phys. Chem. B* **2013**, *117* (49), 15833–15842.
- (34) Tokmakoff, A. Orientational correlation functions and polarization selectivity for nonlinear spectroscopy of isotropic media. II. Fifth order. *J. Chem. Phys.* **1996**, *105* (1), 13–21.
- (35) Tokmakoff, A. Orientational correlation functions and polarization selectivity for nonlinear spectroscopy of isotropic media. I. Third order. *J. Chem. Phys.* **1996**, *105* (1), 1–12.
- (36) Jones, R. Adiabatic change in the Smoluchowski equation: Orientational diffusion of polar particles. *J. Chem. Phys.* **2003**, *119* (3), 1517–1532.
- (37) Nienhuys, H.-K.; Bonn, M. Measuring molecular reorientation at liquid surfaces with time-resolved sum-frequency spectroscopy: A theoretical framework. *J. Phys. Chem. B* **2009**, *113* (21), 7564–7573.
- (38) Zare, R. N. *Angular momentum: Understanding spatial aspects in chemistry and physics*; Wiley-Interscience, 2013.
- (39) Stiopkin, I. V.; Jayathilake, H. D.; Weeraman, C.; Benderskii, A. V. Temporal effects on spectroscopic line shapes, resolution, and sensitivity of the broad-band sum frequency generation. *J. Chem. Phys.* **2010**, *132* (23), 234503.
- (40) Bhattacharyya, D.; Montenegro, A.; Dhar, P.; Mammetkuliye, M.; Pankow, R. M.; Jung, M. C.; Thompson, M. E.; Thompson, B. C.; Benderskii, A. V. Molecular Orientation of Poly-3-Hexylthiophene at the Buried Interface with Fullerene. *J. Phys. Chem. Lett.* **2019**, *10* (8), 1757–1762.
- (41) Wei, X.; Shen, Y. Motional effect in surface sum-frequency vibrational spectroscopy. *Phys. Rev. Lett.* **2001**, *86* (21), 4799.
- (42) Rothschild, W. G. Motional characteristics of large molecules from their Raman and infrared band contours: vibrational dephasing. *J. Chem. Phys.* **1976**, *65* (1), 455–462.
- (43) McHale, J. L. *Molecular spectroscopy*, 1st ed.; Prentice Hall: Upper Saddle River, NJ, 1999.
- (44) Brown, R. D.; Hund, Z. M.; Campi, D.; O'Leary, L. E.; Lewis, N. S.; Bernasconi, M.; Benedek, G.; Sibener, S. J. The interaction of organic adsorbate vibrations with substrate lattice waves in methyl-Si (111)-(1×1). *J. Chem. Phys.* **2014**, *141* (2), 024702.
- (45) Breen, P.; Warren, J.; Bernstein, E.; Seeman, J. I. A study of nonrigid aromatic molecules by supersonic molecular jet spectroscopy. I. Toluene and the xylenes. *J. Chem. Phys.* **1987**, *87* (4), 1917–1926.
- (46) Borst, D. R.; Pratt, D. W. Toluene: Structure, dynamics, and barrier to methyl group rotation in its electronically excited state. A route to IVR. *J. Chem. Phys.* **2000**, *113* (9), 3658–3669.
- (47) Nair, K. R.; Demaison, J.; Włodarczyk, G.; Merke, I. Millimeterwave rotational spectrum and internal rotation in o-chlorotoluene. *J. Mol. Spectrosc.* **2006**, *237* (2), 137–142.
- (48) Kemp, J. D.; Pitzer, K. S. The entropy of ethane and the third law of thermodynamics. Hindered rotation of methyl groups. *J. Am. Chem. Soc.* **1937**, *59* (2), 276–279.
- (49) Jacobsen, S.; Andresen, U.; Mäder, H. Microwave Spectra of o-Fluorotoluene and Its 13 C Isotopic Species: Methyl Internal Rotation and Molecular Structure. *Struct. Chem.* **2003**, *14* (2), 217–225.
- (50) Ferres, L.; Mouhib, H.; Stahl, W.; Nguyen, H. V. L. Methyl Internal Rotation in the Microwave Spectrum of o Methyl Anisole. *ChemPhysChem* **2017**, *18* (14), 1855–1859.
- (51) Rudolph, H.; Walzer, K.; Krutzik, I. Microwave spectrum, barrier for methyl rotation, methyl conformation, and dipole moment of ortho-xylene. *J. Mol. Spectrosc.* **1973**, *47* (2), 314–339.
- (52) Belov, S.; Tretyakov, M. Y.; Kleiner, I.; Hougen, J. T. The second torsional state of acetaldehyde. *J. Mol. Spectrosc.* **1993**, *160* (1), 61–72.
- (53) Kleiner, I.; Hougen, J. T.; Suenram, R.; Lovas, F. J.; Godefroid, M. The ground torsional state of acetaldehyde. *J. Mol. Spectrosc.* **1991**, *148* (1), 38–49.
- (54) Kleiner, I.; Hougen, J.; Suenram, R.; Lovas, F. J.; Godefroid, M. The ground and first torsional states of acetaldehyde. *J. Mol. Spectrosc.* **1992**, *153* (1–2), 578–586.
- (55) Kundu, T.; Pradhan, B.; Singh, B. P. Origin of methyl torsional potential barrier—an overview. *Proc. - Indian Acad. Sci., Chem. Sci.* **2002**, *114* (6), 623–638.
- (56) Welzel, A.; Hellweg, A.; Merke, I.; Stahl, W. Structural and torsional properties of o-cresol and o-cresol-OD as obtained from microwave spectroscopy and ab initio calculations. *J. Mol. Spectrosc.* **2002**, *215* (1), 58–65.