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

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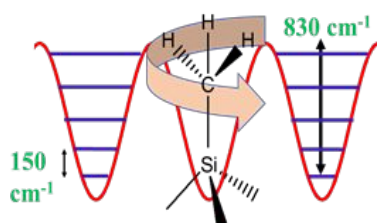
Abstract

The methyl-terminated Si(111) surface possesses a three-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 (VSFG) spectroscopy to determine the rotational relaxation rate of the surface methyl groups and have measured the temperature dependence of the relaxation rate between 20 °C and 120 °C. By fitting the measured rate to an Arrhenius dependence, we extracted an activation energy (the rotational barrier) of 830±360 cm⁻¹ and an attempt frequency of (2.9±4.2)×10¹³ s⁻¹ for the methyl rotation process. Comparison with the harmonic frequency of a methyl group in a 3-fold cosine potential

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3 suggests that the hindered rotation occurs via uncorrelated jumps of single methyl groups rather
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5 than concerted gear-like rotation.
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19 TOC graphic

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3 Functionalized Si(111) surfaces have important applications ranging from inorganic
4 photovoltaics to nanoscale lithography.¹⁻¹⁴ A monolayer of organic adsorbate covalently bonded
5 to the surface Si atoms not only enhances the resistivity of the surface towards air oxidation,^{15,16}
6 but also allows tuning of the chemical reactivity at the surface.⁵ The methyl-terminated Si(111)
7 surface is a singular example of such chemical functionalization, with all of the Si atoms at the
8 topmost layer of the crystalline Si surface being covalently bonded to methyl groups through Si-
9 C bonds. Previous theoretical¹⁷⁻¹⁹ and experimental studies²⁰⁻²⁴ have shown that these terminal
10 methyl groups are oriented perpendicular to the Si substrate. Use of a two-step
11 halogenation/methylation process via Grignard chemistry^{5,15,16} enables nearly 100% coverage of
12 methyl groups on the atop Si atoms, resulting in a well-ordered, densely-packed, chemically
13 well-defined organic monolayer. Steric interactions between the adjacent methyl groups may
14 hinder the rotation of $-CH_3$ groups along the Si-C bond, and therefore the orientation of the
15 methyl groups might be interlocked at the interface.⁵
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34 Several groups have studied the three-fold azimuthal anisotropy of Si(111) surfaces by
35 second harmonic generation (SHG) spectroscopy.²⁵⁻²⁷ SHG probes the electronic resonances of
36 the Si substrate and therefore is not sensitive to the attached chemical groups. In contrast,
37 vibrational sum frequency generation (VSFG) spectroscopy has provided information about the
38 covalently attached functional groups on methyl-terminated²⁸ and propynyl-terminated Si(111)
39 substrates.²⁹ Along with the three-fold anisotropy of the Si(111) surface probed by SHG
40 spectroscopy, a three-fold rotational anisotropy of covalently attached methyl and propynyl
41 groups has been observed by VSFG spectroscopy, corroborating the proposition by Yamada
42 et.al.⁵ that the orientation of the methyl groups is interlocked at the interface due to steric
43 interactions with the neighboring ligands. Line-shape analysis of VSFG spectra has also
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3 revealed that methyl groups on the methyl-terminated Si(111) surface undergo hindered rotation
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5 between the three isoenergetic equilibrium orientations at the interface.²⁸
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9 In this work, we used surface-selective VSFG spectroscopy to investigate the energy
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11 barrier of the hindered rotation of methyl groups of the methyl-terminated Si(111) surface.
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13 Methyl-terminated Si(111) surfaces were prepared and characterized as described previously.³⁰⁻³²
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15 To remove impurities, the samples were rinsed with water, acetone, methanol and again with
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17 water, and were heated in vacuo overnight at 450 °C. VSFG experiments before and after
18
19 annealing the sample indicated that additional peaks associated with -CH₂ vibrational
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21 frequencies disappeared upon annealing, and are thus consistently ascribed to impurities. A
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23 broadband femtosecond IR pulse centered around 3000 cm⁻¹ with a FWHM of ~250 cm⁻¹ was
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25 used to excite the symmetric and asymmetric stretching modes of the methyl groups. A
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27 narrowband picosecond 800 nm pulse upconverted the coherences, and the sum-frequency light
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29 was collected in the phase-matching direction. VSFG spectra were collected for two different
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31 polarization combinations of input and output beams: PPP and SPS, where the polarizations of
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33 the output SFG field and the input visible and IR fields are written from left to right. The sample
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35 was kept on top of a Peltier cooling/heating element that was glued over a water-cooled Al
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37 block, to allow measurement of VSFG spectra at five different temperatures between 20 °C and
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39 120 °C. The sample chamber was continuously purged with dry air during the experiment. A
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41 thermocouple as well as an IR heat sensor were used to measure the temperature of the sample.
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49 Infrared spectroscopy measurements of the methyl-terminated Si(111) samples showed
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51 characteristic peaks for the symmetric and asymmetric stretches of the methyl groups at 2910
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53 cm⁻¹ and 2975 cm⁻¹, respectively.^{20,21} Figure 1 shows the VSFG spectra for PPP and SPS
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55 polarizations. In the case of PPP polarization, two peaks were present, corresponding to the two
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3 IR active modes of methyl groups; for SPS polarization, the peak corresponding to the
4 symmetric stretching vibration was absent. The methyl groups are oriented perpendicular to the
5
6 symmetric stretching vibration was absent. The methyl groups are oriented perpendicular to the
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8 Si(111) substrate, so the transition dipole of the symmetric stretch (along its C_{3v} symmetry axis)
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10 is also perpendicular to the surface, whereas the transition dipole of the asymmetric stretch lies in
11
12 the plane of the silicon substrate. As a result, S-polarized IR light, with the polarization in the
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14 plane of the substrate, cannot couple with the transition dipole of the symmetric stretch, but can
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16 couple with the transition dipole of the asymmetric vibrational stretch. The large sloping
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18 response in the lower frequency side of the SPS spectra comes from the nonlinear non-resonant
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20 background in that region which could not be subtracted properly.
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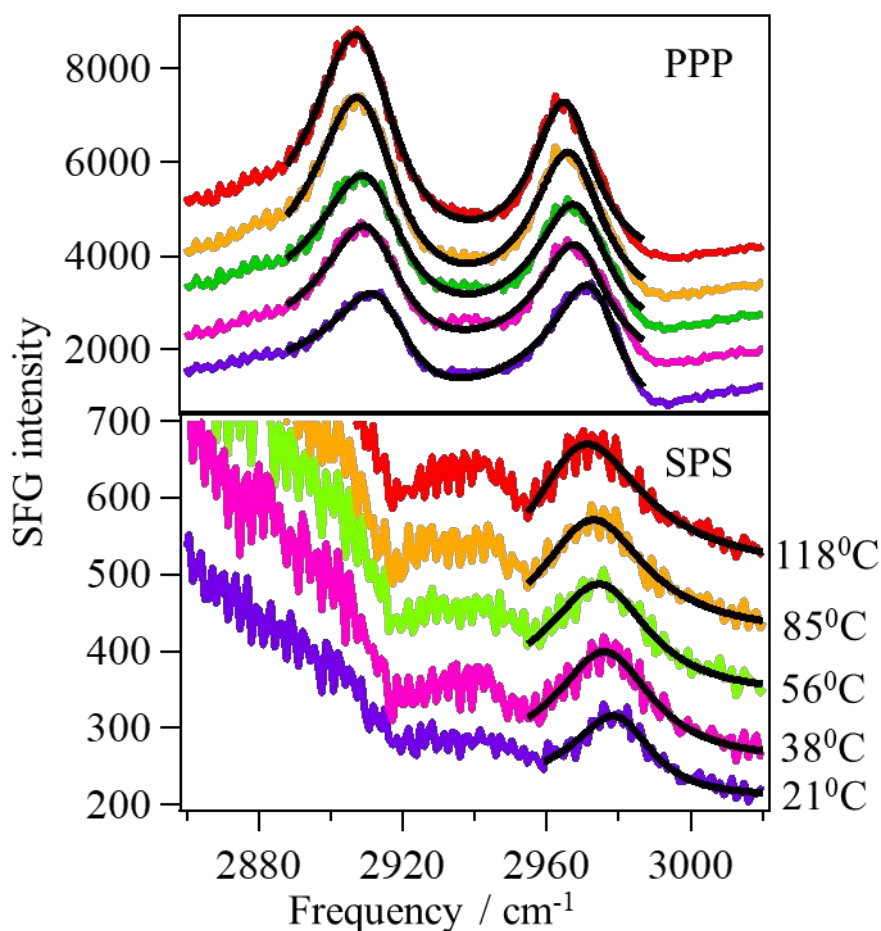


Figure 1: VSFG spectra of methyl-terminated Si(111) for PPP and SPS polarizations measured at five different temperatures. Spectra at different temperatures (blue (21 °C), purple (38 °C), green (56 °C), yellow (85 °C) and red (118 °C)) are stacked vertically, after adding a constant offset to each spectrum.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

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_{\parallel}) 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 re-written as:

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

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

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 reorientation dynamics on the same timescale ($C_3^{PPP} = 0$).³³ The modified response function for PPP polarization is thus:

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

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 (1-3) are the same, with the in-plane diffusion constant (D_{\parallel}) replaced by the rate constant (k_{rot}) of such hindered rotation.

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

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

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

where A is the amplitude and Γ is the HWHM of the Lorentzian. The linewidth of the SPS spectra has contributions from both the vibrational dephasing and in-plane orientation dynamics, whereas the PPP linewidth only has a vibrational dephasing contribution. For methyl-terminated Si(111), the $-\text{CH}_3$ groups are oriented perpendicular 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 linewidth of the PPP spectra, however, is not affected by such rotation. The difference between SPS and PPP linewidth for the asymmetric stretch vibration contains information about the reorientation dynamics of the molecule:^{33, 39}

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

Figure 1 also shows the SFG spectra of the $H_3C-Si(111)$ surface measured at five different temperatures. The SFG spectra were fitted using the following equation:⁴⁰

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

where A_{NR} and φ are the amplitude and phase, respectively, of the non-resonant 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 increasing temperature, whereas Γ_{PPP} did not show a substantial change between 20 °C and 90 °C, with however a noticeable decrease in linewidth above 90 °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 linewidth. 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 linewidth at higher temperature could be due to motional narrowing.^{41,42}

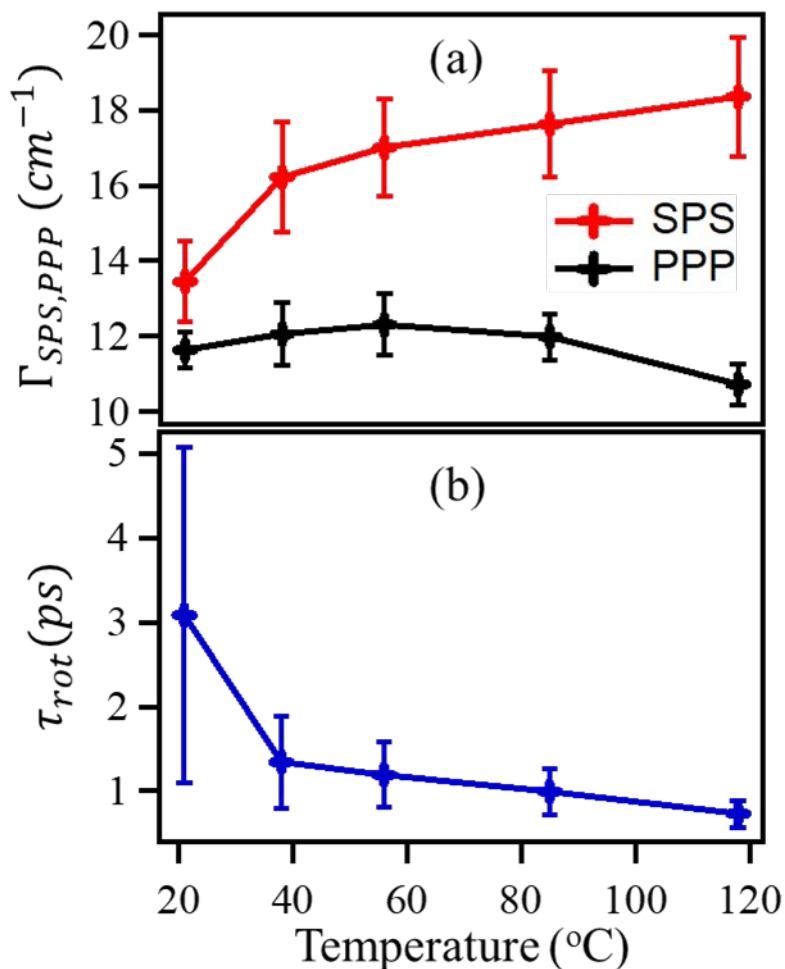


Figure 2: Plot of (a) PPP and SPS linewidths of the asymmetric $-\text{CH}_3$ stretch frequency vs. temperature; (b) rotational relaxation timescale vs. temperature.

Following equation 6, k_{rot} (in cm^{-1}) can be calculated at every temperature and assuming the Lorentzian spectral line shape, the timescale 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 °C, the rotational relaxation

timescale is 3 ± 2 ps, whereas, at $118\text{ }^{\circ}\text{C}$, 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 timescale of $\tau_{\text{rot}} = 1\sim 2$ ps. Use of a classical correlation function⁴³ for the free-rotors predicts that the timescale 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 shows the natural logarithm of the rate constant, $\ln(k_{\text{rot}})$ plotted against $1/T$ according to Arrhenius equation:

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

where T is the temperature in Kelvin; E_{rot} is the activation energy, which in our case, is the barrier of methyl rotation; and 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. $112\text{ meV} \sim 900\text{ cm}^{-1}$, 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 $\sim 1000 \text{ cm}^{-1}$ (ethane)⁴⁸ (Table 1). The attempt frequency (k_0) can be calculated from the 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 $\text{CH}_3\text{-Si}(111)$, which corresponds to a frequency of 150 cm^{-1} for the restricted rotation.

Table I: Torsional barrier of methyl groups in different organic compounds tabulated from the literature.

Compound	Methyl rotational barrier (cm^{-1})
Toluene	$10^{45,46}$
o-fluorotoluene	227^{49}
³⁵ Cl-o-chlorotoluene	514^{47}
³⁷ Cl-o-chlorotoluene	507^{47}
o-methylanisole	444^{50}
o-xylene	518^{51}
Acetaldehyde	408^{52-55}
anti-o-cresol	370^{56}
syn-o-cresol	661^{56}
methylsilane	500^{44}
ethane	1100^{48}

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 threefold symmetric potential can be written in the form: $V(\varphi) = \frac{1}{2}E_{rot}(1 - \cos(3\varphi))$;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 compared to the rotational barrier, i.e. $k_B T \ll E_{rot}$, yields an expression for the harmonic frequency (ν) of the torsional motion as:⁴³

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

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 $E_{rot} = 9.9 \text{ kJ/mole}$, 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.

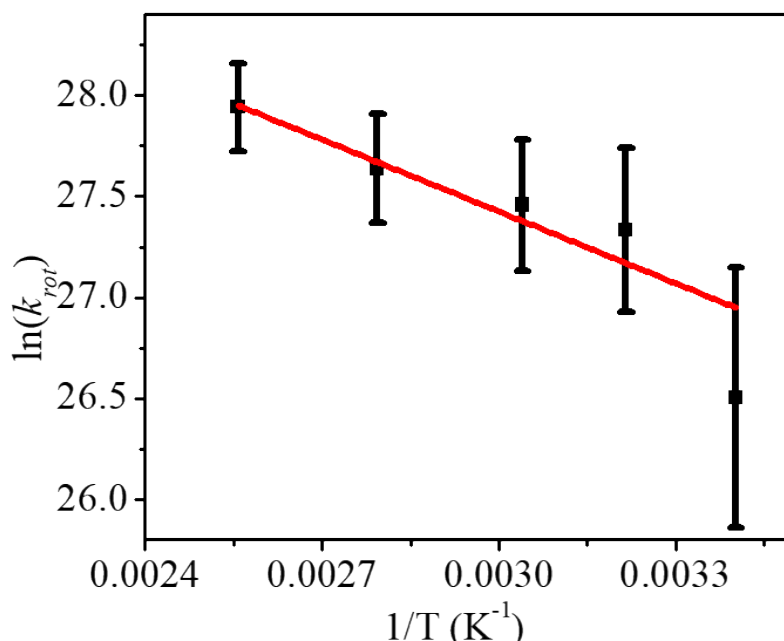


Figure 3: $\ln(k_{rot})$ vs $1/T$ plot; where k_{rot} is the rotational rate constant and T is the temperature in Kelvin. The plot is fitted with a straight line (red). The slope and the intercept of the fitted line are used to calculate the rotational barrier (E_{rot}) and the attempt frequency (k_0).

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3 Similar experiment can be done for CD₃-Si(111) system. Brown et al.⁴⁴ reported the
4 frequency of the hindered methyl rotation to be 29.0 meV ~ 234 cm⁻¹ for CH₃-Si(111) and 20.8
5 meV ~ 168 cm⁻¹ for CD₃-Si(111) at the $\bar{\Gamma}$ -point. Deuteration of the methyl groups thus results
6 into decreasing the attempt frequency of the rotational motion by a factor of $(\sqrt{2})^{-1}$ and also,
7 lowers the zero-point energy along the torsional vibrational coordinate. As a consequence, the
8 rotational activation barrier of the methyl groups for a CD₃-Si(111) system will be higher as
9 compared to that of CH₃-Si(111) system. It is to point out that resonant vibrational energy
10 transfer can happen via coupling of the transition dipoles between neighboring methyl groups
11 and it is one of the possible mechanisms for orientational dephasing in methyl terminated
12 silicon(111) surfaces. Isotopic dilution of CH₃-Si(111) substrate effectively gives us a tool to
13 tune such dipole-dipole coupling which directly influences the vibrational and rotational
14 dephasing. Therefore, using a mixed layer of CH₃ and CD₃ terminated Si(111) surface or a
15 highly diluted CH₃-Si(111) surface will be a classic way to decouple different dephasing
16 channels. One practical problem will be to record the SPS spectra for the isotopically diluted
17 samples because of its considerably low signal to noise.
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38 Conclusions

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43 We have used VSFG spectroscopy to determine the rotational barrier of methyl groups of
44 the methyl-terminated silicon(111) surface. The methyl groups are oriented perpendicular to the
45 Si substrate and cannot rotate freely due to steric interactions with the adjacent methyl moieties.
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47 As a result, the VSFG response from the C-H stretches of the methyl groups showed a three-fold
48 rotational anisotropy. The room temperature PPP vs SPS line-shape analysis predicts a
49 possibility of hindered rotation of the methyl groups between three isoenergetic equilibrium
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3 configurations. For a “rod-like molecule” standing perpendicular to the substrate and rotating
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5 with respect to the surface normal, the PPP spectral line-shape is mainly dominated by the
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7 vibrational relaxation, whereas the SPS spectrum carries information about both the vibrational
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9 dephasing and rotational dynamics. Increasing temperature results in faster rotational relaxation,
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11 which manifests itself in the increase in SPS linewidth. Therefore, the difference between SPS
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13 and PPP linewidth increases with temperature and measures the contribution of the reorientation
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15 dynamics in the VSFG spectra for CH₃-Si(111) surface. Fitting the rate constant of rotational
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17 relaxation (k_{rot}) to the Arrhenius equation yields the energy barrier of rotation, $E_{rot} =$
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19 $830 \pm 360 \text{ cm}^{-1}$, as well as the attempt frequency, $k_0 = 2.9 \times 10^{13} \text{ s}^{-1}$. The experimentally
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21 determined attempt frequency matches well with the calculated harmonic torsional frequency of
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23 a single methyl group. This accord suggests that the methyl rotation on the CH₃-Si(111) surface
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25 is not a concerted gear-like motion involving multiple methyl groups but rather represents the
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27 rotation of an individual methyl group uncorrelated from the rest of the surface functionality.
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29 This work thus demonstrates a unique application of VSFG spectral line-shape analysis to
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31 visualize the mechanistic details of a hindered methyl rotation on a methyl-terminated Si(111)
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33 surface.
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41 **Experimental methods**

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43 A dual-stage Ti-Sapphire amplifier system operating at a 5 kHz repetition rate and
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45 generating a femtosecond 800 nm pulse with a pulse energy of 3 mJ was used to generate the
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47 light pulses for VSFG spectroscopy. One portion of the amplifier output (pulse width of ~40 fs
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49 and pulse energy of 1.5 mJ) as used to pump the TOPAS optical parametric amplifier (OPA).
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51 The outputs from the OPA (signal and idler) were routed to the noncollinear difference
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53 frequency generator (NDFG) to generate a broadband mid-infrared pulse centered around 3000
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3 cm⁻¹ with a bandwidth of 250 cm⁻¹. The other portion of the amplifier output was first externally
4 compressed using a grating compressor and then passed through a 4f stretcher to narrow the
5 pulse in frequency domain and produce a boxcar spectral profile. The frequency resolution was
6 achieved by this picosecond 800 nm up-conversion pulse (FWHM ~8-10 cm⁻¹). At the sample,
7 the power of the IR light was 4 μJ/pulse and that of the visible light was 7 μJ/pulse. The spot-size
8 of the IR and the visible beams were 190 μm and 230 μm respectively. The angle of incidence of
9 the visible and the IR beam was 67° and 62° with respect to the surface normal. The SFG spectra
10 were recorded using a liquid-nitrogen-cooled CCD detector (2048 × 512 pixels). To perform
11 temperature dependent experiments, a commercial Peltier cooler (MARLOW Industries, Model
12 no: RC12-8L) was purchased and glued over a hollow Al block through which room temperature
13 water was flowed by an external pump. The sample was kept on top of that Peltier
14 cooling/heating element. A voltage vs temperature calibration plot was created by changing the
15 input voltage of the Peltier cooler and measuring the temperature of the sample using a
16 thermocouple as well as an IR heat sensor. The sample chamber was continuously purged with
17 dry air during the experiment.
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37 38 **Acknowledgments**

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49 **Supporting Information Available**

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51 Experimental details, Spectral fitting parameters of SFG data.
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