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S Supporting Information

ABSTRACT: A rotationally fluid state of α -pinene at fused silica/vapor interfaces is revealed by computational and experimental vibrational sum frequency generation (SFG) studies. We report the first assignment of the vibrational modes in the notoriously congested C–H stretching region of α -pinene and identify its bridge methylene group on the four-membered ring (" $^{\beta}$ CH₂") as the origin of its dominant spectral feature. We find that the spectra are perfused with Fermi resonances that need to be accounted for explicitly in the computation of vibrational spectra of strained hydrocarbons such as α -pinene. The preferred orientations of α -pinene are consistent with optimization of van der Waals contacts with the silica surface that results in a bimodal distribution of highly fluxional orientations in which the $^{\beta}$ CH₂ group points "towards" or "away from"



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the surface. Classical molecular dynamics simulations further provide rotational diffusion constants of 49 ± 1 ps and 2580 ± 60 ps, which are attributed to two broad types of adsorption modes on silica. The reported findings are particularly relevant to the exposure of α -pinene to primary oxidants in heterogeneous catalytic pathways that exploit α -pinene as a sustainable feedstock for fine chemicals and polymers.

I. INTRODUCTION

 α -Pinene is an important species in the earth's climate system,¹ where it participates in the formation of secondary organic aerosols (SOAs) by ozonolysis. α -Pinene also plays a major role in interspecies signaling,² and it can serve as a sustainable feedstock for polymer synthesis^{3–5} and fine chemicals.^{6–8}

Many of the physical and chemical processes involving α pinene conversions occur heterogeneously,⁵ including in environments formed by organic frameworks^{4,9,10} and mesoporous materials.^{4,6–8,10,11} It is, in principle, possible to track α pinene at gas/solid or liquid/solid interfaces using vibrational spectroscopy. Yet, the spectral assignments are challenging to obtain in a reliable fashion because the vibrational spectra of α pinene are congested. This is especially the case in the C–H stretching region, where Fermi resonances can strongly modulate the intensity and energy of the vibrational bands. While experimental and theoretical IR and Raman spectra of α pinene have been reported for quite a while now (the first report by Wilson dates as far back as 1976),^{12–14} the assignments of the vibrational bands have not yet been evaluated using methods that account for Fermi resonances and other nonlocal modes. Here, we use *ab initio* methods and molecular dynamics simulations to show that nonlocal modes are critical for understanding the vibrational spectra of α pinene. To do so, we simulate, while accounting for Fermi resonances, vibrational sum frequency generation (SFG) spectra of α -pinene. Unlike its infrared or Raman counterparts in the bulk gaseous or liquid phases, SFG is a second-order process that often produces superior spectral resolution and less broadened spectral features compared with first-order spectra, especially at room temperature.^{15–21} This gain in spectral resolution is key for testing how important Fermi resonances are for assigning the vibrational spectra of α -pinene and, by extension, other terpenes. Moreover, the spectra inform on the symmetry of the vibrational modes and therefore molecular orientation,^{15–17,22} which we address here as well.

Given that the SFG process is forbidden in centrosymmetric environments, the method requires α -pinene be adsorbed at a

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surface. Here, we characterize the interaction of α -pinene with fused silica, which we chose for its optical properties in the infrared and the visible spectral range (work with α -quartz and CaF_2 is ongoing and will be reported in due course) and for its relevance to mesoporous oxide materials used in α -pinene transformations. Only four vibrational modes of α -pinene have been previously assigned in an earlier study by us.²³ Here, we apply *ab initio* methods to assign all of the vibrational modes in the C-H stretching region while explicitly accounting for Fermi resonances and nonlocal modes. We employ density functional theory (DFT) for calculations of SFG spectra in conjunction with classical and density-functional tight-binding (DFTB) molecular dynamics (MD) simulations and hybrid ONIOM(MO:MO) calculation for characterization of the α pinene/silica interactions. The reported characterization through direct comparisons with experimental data on the α pinene/silica system provides not only fundamental insights on the nature of surface adsorption of an important species in nature and technology but also a benchmark of a methodology that we envision should be useful for modeling complex hydrocarbons physisorbed to various solids.

Simulations of vibrational SFG spectra have proven to be useful to interpret experimental results for various interfacial systems.^{24–39} MD simulations, in particular, are helpful for determining distributions of molecular orientations at interfaces.^{24–26,40–43} Ab initio and classical MD simulations have also been implemented for simulations of the SFG spectra of biomolecules such as leucine adsorbed to polystyrene in the C– H stretching region.⁴⁴ While that work did account for Fermi resonances by making amplitude corrections, a general method for taking these resonances into account using a Hamiltonian was not presented. Here, we combine methods to elucidate the characteristic vibrational modes that contribute to the SFG spectrum of α -pinene at the vapor/fused silica interface by explicitly including Fermi resonances through an appropriately modeled Hamiltonian.

II. METHODS

II.A. Experimental Methods. The sub-1 cm⁻¹ SFG spectrometer used for the experiments discussed here has been described thoroughly in recent work, 21,23,45,46 and the reader is referred to those references for a detailed explanation. Briefly, the high resolution is achieved through the synchronization of two 1 kHz regeneratively amplified Ti:sapphire lasers, implemented at Pacific Northwest National Laboratory. The SFG spectrum provided here was taken at the vapor/fused silica interface using the ssp-polarization combination (spolarized SFG, s-polarized visible, and p-polarized IR). The experiment was carried out by placing a few drops of neat (-)- α -pinene into a shallow Teflon beaker, which was subsequently covered with an IR-grade fused silica optical window that was 3 mm thick and 25.4 mm in diameter. The spectrum shown is an average of three individual spectra each acquired for 10 min.

I.B. Computational Methods. *II.B.1. Coordinate System Transformation.* The intensity of the SFG spectrum is proportional to the square modulus of the nonlinear susceptibility, $\chi^{(2)}$,

$$I_{\rm SFG} \propto |\chi^{(2)}|^2 \tag{1}$$

where $\chi^{(2)}$ consists of a resonant component and nonresonant component. The nonresonant component is neglected, because the baseline of our spectrum is close to zero. Computationally, the resonant term $\chi^{(2)}$ is a macroscopic average of elements from the first-order hyperpolarizability tensor, β_{abc} . The hyperpolarizability tensor

$$\boldsymbol{\beta}_{abc,q} \propto \frac{\partial \alpha_{ab}}{\partial Q_q} \frac{\partial \mu_c}{\partial Q_q} \tag{2}$$



Figure 1. (A) Molecular coordinate orientation of α -pinene. (B) Atomic labeling for α -pinene.

is constructed for each normal mode, from the Raman polarizabilites, $\frac{\partial \alpha_{ab}}{\partial Q_q}$, and the dipole moment derivatives $\frac{\partial \mu_i}{\partial Q_q}$ relative to the normal mode coordinate Q. In order to compute spectra for a variety of orientations, we establish a set of molecular coordinates (a, b, c), as shown in Figure 1.

The molecular coordinates were set so that the origin is coincidental with the bridging tetrahedral carbon bonded to the ${}^{\chi}CH_3$ and ${}^{\eta}CH_3$ groups (please refer to Figure 1 for the use of the superscripts identifying the three methyl groups). Using this coordinate origin, the *c*-axis is collinear with the C–C bond corresponding to the ${}^{\chi}CH_3$ group, the *a*-axis is orthogonal to the *c*-axis and is directionally aligned with the ${}^{\eta}CH_3$ group, and the *b*-axis is orthogonal to the *a*-axis and *c*-axis. From the molecular coordinates, the hyperpolarizabilities are rotated using a transformation matrix to the laboratory frame of coordinates (*i*, *j*, *k*). The generalized second order susceptibility is

$$\chi_{ijk,q}^{(2)} = N_{\rm s} \sum_{a,b,c} \langle R_{ia} R_{jb} R_{kc} \rangle \beta_{abc,q}$$
(3)

where N_s is the surface density of molecules and **R** is the rotational transformation matrix, which is used to convert from the molecular coordinates into laboratory coordinates. The Euler rotational transformation matrix used in this study is the ZYZ rotation matrix,⁴⁷

$$Z_{\phi}Y_{\phi}Z_{\psi} = \begin{pmatrix} \cos\phi\cos\theta\cos\psi - \sin\phi\sin\psi & -\cos\phi\cos\theta\sin\psi - \sin\phi\cos\psi & \cos\phi\sin\theta\\ \sin\phi\cos\theta\cos\psi + \cos\phi\sin\psi & -\sin\phi\cos\theta\sin\psi + \cos\phi\cos\psi & \sin\phi\sin\theta\\ -\sin\theta\cos\psi & \sin\theta\sin\psi & \cos\theta \end{pmatrix}$$
(4)

which is based on the tilt angle (θ), twist angle (ψ), and spin angle (ϕ) . To determine the orientations yielding the bestmatching spectrum, we sampled orientations with a grid of ca. 1300 points corresponding to all θ and ψ angles for every 10° between 0° and 360°. We assume zero net orientation of the α pinene molecules within the x-y plane and average the azimuthal angle ϕ between 0° and 360° for each set of (θ, ψ) angles over 5° increments so as to reflect the lack of rotational anisotropy of the substrate. Specifically, we utilize the ssppolarization combination, which probes vibrational transition dipole moment components oriented parallel to the surface normal that are encoded in the $\chi^{(2)}_{xyz}$ nonlinear susceptibility element. What is ultimately computed is proportional to the square modulus of the *effective* nonlinear susceptibility, $\chi^{(2)}_{ssn}$ which we express as a linear combination of nonlinear susceptibilities. Particularly relevant to this experiment, we compute

$$I_{\rm SFG} \propto |\chi_{\rm ssp}^{(2)}|^2 I_{\rm vis} I_{\rm IR} \tag{5}$$

where

$$\chi_{\rm ssp}^{(2)} = L_{yy}(\omega_{\rm SFG})L_{yy}(\omega_{\rm vis})L_{zz}(\omega_{\rm IR})\sin\alpha_{\rm IR}\chi_{yyz} \tag{6}$$

In this expression, *L* are the Fresnel coefficients, and $\alpha_{\rm IR}$ is the incident angle of the IR beam.

II.B.2. Accounting for Fermi Resonances. Vibrational modes corresponding to C–H stretching motions of α -pinene densely populate the frequency range from 2800 to 3050 cm⁻¹. Many of the vibrational modes in this region are split due to Fermi resonance coupling with combination and overtone bands of lower energy vibrational modes. Fermi resonance splittings for each fundamental vibrational mode were computed by diagonalizing a matrix constructed from the fundamental mode energy and all combination and overtone bands with the corresponding coupling terms,⁴⁸

$$\mathbf{H} = \begin{cases} \omega_i & \gamma_{i1} & \gamma_{i2} & \cdots \\ \gamma_{i1} & \omega_1 & 0 & \cdots \\ \gamma_{2i} & 0 & \omega_2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{cases}$$
(7)

where ω_i is the energy of the fundamental mode, ω_n (n = 1, 2, 3, 4, etc.) are the energies of the combination bands and overtones within a designated energy threshold of the fundamental mode, and γ_{in} are the coupling terms associated with each resonance.

All electronic structure calculations were carried out using Gaussian 09 software.⁴⁹ Density functional theory was used for all computations at the B3LYP level of theory⁵⁰⁻⁵³ using the 6-311++G(d,p) basis set.^{54,55} Geometry optimizations with a tight optimization criteria and default grid were performed on α -pinene followed by harmonic vibrational frequency analysis to compute normal mode frequencies and confirm that it is a minimum structure. Anharmonic vibrational frequency calculations were performed along with harmonic vibrational frequency calculations to obtain the combination and overtone bands in Fermi resonance with fundamental vibrational frequencies. Harmonic dipole derivatives with respect to each vibrational normal mode were calculated in tandem with the vibrational frequency calculations, but displayed in the output file using the Gaussian09 keyword "iop(7/33 = 1)". Polarizability tensors with respect to each vibrational normal mode

were obtained using the "polar" keyword. Simulated vSFG spectra were created by applying Lorentzian line shapes over calculated intensities with a full width at half-maximum (fwhm) of 5 cm⁻¹ effectively modeling the broadening effects present in experimental vSFG spectra that are observed between 3100 and 2700 cm⁻¹.

II.B.3. Scaling. In addition to the Fermi resonance treatment described in eq 7, all harmonic vibrational frequencies and split bands need to be scaled for proper comparison to an experimental spectrum. A uniform scaling factor of 0.957 was determined for the C–H stretching region by manually adjusting the placement of the vibrational modes for optimal overlap with the experimental spectrum. The determined scaling factor is consistent with typical vibrational frequency scaling factors for this level of theory.^{56–58} Calculated (scaled) vibrational frequencies for α -pinene are tabulated in Table 1, and the labels for the various CH groups are shown in Figure 1B.

Table 1. Vibrational Normal Mode Frequencies in cm⁻¹ with Fermi Resonance Combination Bands for α -Pinene

vibrational mode ^a	frequency ^b [cm ⁻¹]	mode description		
mode 57 $EP(4)$ of	2849	$ ho {\rm CH_2}$ symmetric stretch		
mode 57	2801-2882			
mode 58	2872	νCH_3 symmetric stretch		
FR(1) of mode 58	2876			
mode 59	2880	$ ho \mathrm{CH}_2$ antisymmetric stretch		
mode 60	2858	η_{χ} CH ₃ symmetric stretch (asynchronous)		
FR(4) of mode 60	2880-2910			
mode 61	2862	η_{χ} CH ₃ symmetric stretch (synchronous)		
FR(4) of mode 61	2885-2924			
mode 62	2910	bridging CH ($ ho$ adjacent) stretch		
mode 63	2910	νCH ₃ asymmetric stretch		
mode 64	2921	bridging CH (vinyl) stretch		
mode 65	2929	η_{χ} CH ₃ asymmetric stretch (asynchronous)		
mode 66	2929	$\beta \mathrm{CH}_2$ symmetric stretch		
FR(1) of mode 66	2934			
mode 67	2937	η_{χ} CH ₃ asymmetric stretch (synchronous)		
mode 68	2958	νCH_3 asymmetric stretch		
mode 69	2967	$\eta \mathrm{CH}_3$ asymmetric stretch		
mode 70	2986	χCH_3 asymmetric stretch		
mode 71	2988	$\beta \mathrm{CH}_2$ antisymmetric stretch		
mode 72	3004	vinyl CH stretch		
a "FR(X) of mode Y	refers to the	X Fermi resonance of mode Y		
^b Calculated vibrational frequencies were scaled by 0.957.				

ll.B.4. Trajectory Calculations. Classical MD simulations were performed on a model of amorphous silica surface based on a 115 × 115 × 20 Å³ slab adopted from the work of Cruz-Chu et al.⁵⁹ We employed CHARMM force field parameters for amorphous silica that have been optimized to reproduce the water contact angle (denoted by CWCA FF).⁵⁹ This force field has also been successfully applied to simulate amorphous silica surfaces,⁶⁰ quartz(1011)–water interfaces,⁶¹ and ionic transport in silica channels.⁶² The intramolecular and intermolecular



Figure 2. (A) Normalized contour plot of the sum of square differences (top) between the calculated and experimental spectra based on rotation angles θ and ψ . The contours are colored in a visible color spectrum where violet and red indicate best and worst agreement with experiment, respectively. Orientations for (B) ($\theta = 0^\circ, \psi = 0^\circ$) and (C) ($\theta = 180^\circ, \psi = 0^\circ$) correspond to overall best-matching orientations of α -pinene (see text). (D) Normalized simulated vSFG spectra for Euler angles ($\theta = 0^\circ, \psi = 0^\circ$, red) and ($\theta = 180^\circ, \psi = 0^\circ$, blue) compared with the experimental spectrum (gray).

parameters are summarized in Tables S1 and S2 in the Supporting Information, respectively.

All dangling oxygen atoms and under-coordinated silicon atoms were capped with hydrogen atoms and hydroxyl groups, respectively. Additionally, each four-membered ring was opened and capped by the addition of a single water molecule forming a vicinal silanol unit to obtain the desired concentration of silanol groups on a silica surface, which typically ranges from 2.6 to 4.6/nm^{2.63} Our model of the silica surface had a surface [Si–OH] concentration of 4/nm². The exact concentration of α -pinene adsorbed onto the silica surface is not known. We have assumed a surface concentration of [α pinene] = 1/nm² for our classical MD simulations. This corresponds to a total of 130 α -pinene molecules on our model silica surface.

The initial force field parameters for α -pinene were generated via the CGenFF/ParamChem engine.⁶⁴⁻⁶⁶ The atomic charges were refined using the Force Field Toolkit plugin⁶⁷ as implemented in VMD.⁶⁸ The final atomic charges for α -pinene are provided in Table S3. All MD simulations were carried out using the NAMD program.⁶⁹ The α -pinene molecules were randomly positioned on the hydroxylated surface and the entire system was minimized for 5000 steps. The system was then equilibrated for 2 ns before a production run of 10 ns, yielding a distribution of orientations from the 130 α -pinene molecules. Simulations were performed with an integration time step of 1 fs and periodic boundary conditions at 300 K. Intermolecular van der Waals interactions were calculated with a cutoff of 12 Å (switching function starting at 10 Å), and long-range electrostatic forces were calculated using the PME summation method. The Langevin thermostat was used to maintain a

constant temperature in the NVT ensemble. The elementary cell extension of the system was $115 \times 115 \times 115 \text{ Å}^3$ where the periodicity along the z-axis was increased deliberately to create 95 Å of empty space above the surface. To keep the amorphous slab rigid, the silica atoms were fixed at their minimized positions during the MD simulation. In order to obtain the trajectory-averaged spectrum of an individual α -pinene, a rotation matrix that aligns the α -pinene at the reference orientation in Figure 1A to the α -pinene orientation in each frame of the trajectory was applied to the hyperpolarizability tensor at the reference orientation. The rotation matrices were computed via the Kabsch algorithm as implemented in VMD.68 Effectively, this algorithm generates the hyperpolarizability tensor and thus a vSFG spectrum at each step of the trajectory. Each trajectory frame of a given α -pinene molecule is isotropically averaged during the MD simulation in the same way as described above. Each isotropically averaged spectrum was further averaged over all frames from the MD simulation (sampled at 1 ps interval) to obtain a trajectory-averaged spectrum as a function of simulation time for that α -pinene molecule. Finally, we arrive at the ensemble-averaged spectrum by averaging over the trajectory-averaged spectra for our ensemble of 130 α -pinene molecules.

Density-functional tight-binding (DFTB)⁷⁰ MD simulations were further carried out on a single α -pinene molecule interacting with a (252-atom) cluster model of fused silica to generate a 50 ps trajectory at 300 K. These simulations were carried out using the DFTB+ program.⁷¹ A bowl-shaped cluster model was carved out from the silica slab used in the classical MD simulations, and the dangling bonds at the periphery of the cluster were capped with hydrogen atoms. Snapshots from the

trajectory were subject to two-layer ONIOM(ω B97XD/6-31G(d):HF/3-21G)^{72,73} optimization to locate the most favored α -pinene orientation on silica. The "high-layer" is composed of α -pinene as well as surface silica atoms so that the surface interactions are treated at the DFT level of theory, and the remainder of the cluster model is treated at the HF/3-21G level (the "low-layer"). All peripheral capping hydrogen atoms are frozen during the optimization in order to preserve the shape of the cluster model. The ONIOM calculations were carried out in Gaussian09.⁴⁹

II.B.5. Rotational Diffusion Calculations. The rotational reorientation time was calculated using the reorientational autocorrelation function,⁷⁴

$$C(t) = \langle P_2(\vec{n}(0) \cdot \vec{n}(t)) \rangle \tag{8}$$

where P_2 is the second Legendre polynomial, $P_2(x) = 1/2(3x^2 - 1)$, $\vec{n}(t)$ is the unit vector shown in Figure 4A at time *t*, and the brackets indicate the average along a 10 ns trajectory. The autocorrelation function is computed for each of the 130 α -pinene molecules in the classical MD trajectory, and the final C(t) is averaged over all α -pinene molecules.

III. RESULTS AND DISCUSSION

III.A. Accounting for Fermi Resonances Improves the Agreement between Calculated and Experimental SFG Spectra of α -Pinene. SFG spectra depend not only on the number of oscillators sampled but also on their molecular orientations, averaged over all orientations. One way to account for the latter is to determine the most probable molecular orientation of the molecule from experiment, which is possible if the symmetry of the vibrational modes contributing to each spectral feature is known.^{15,16,20,75} In this case, one can use the polarization null-angle analysis method^{76-81'} or the ppp/ssp amplitude ratio,⁸²⁻⁸⁵ which is straightforward for molecules lacking significant contributions of Fermi resonances, combination bands, or other nonlocal modes. As we show in this section that the SFG responses from α -pinene and the orientation distributions giving rise to them cannot be described satisfactorily unless Fermi resonances and combination bands are included.

Below, we use two DFT-based methods to estimate the most likely orientation of α -pinene that gives rise to the experimentally observed SFG responses. As described in the Methods section, the first method is based on (1) a zerointeraction potential between an α -pinene molecule hovering over a hypothetical flat surface at all hypothetical molecular orientations above the surface, (2) computation of the SFG spectrum, (3) comparison of the sum of squared differences between the normalized calculated and experimental spectra, and (4) identification of the best spectral match, which identifies the molecular orientation.^{30,86} The second method incorporates steps 1-4 of the first method but includes explicit interaction dynamics by updating the hyperpolarizability tensor (through rotation) at each step of a classical MD simulation. As described in the Methods section, the latter method yields not only orientation data but also information regarding the interaction dynamics and energetics.

Using the first method, we obtained a normalized error contour map between the calculated and experimental spectra as presented in Figure 2A. The normalized error at a specific orientation (θ , ψ) is defined as (SSD – SSD_{min})/(SSD_{max} – SSD_{min}) where SSD_{min} (SSD_{max}) is the minimum (maximum) sum of squared differences. Regions marked in blue correspond

to small errors and are found for a wide range of ψ angles near $\theta = 0^{\circ}$ and $\theta = 180^{\circ}$. At these orientations, the $C^{-\chi}C$ axis is aligned approximately orthogonal to the surface. Note also that for a given θ , varying ψ corresponds to spinning the molecule around the surface normal. Figure 2B,C shows the molecular orientation at selected points along these axes $(\theta, \psi) = (0^{\circ}, 0^{\circ})$ and $(180^{\circ}, 0^{\circ})$. Figure 2D shows the calculated SFG spectra at the orientations in Figure 2B,C, along with the experimental SFG spectrum. Just like in the experimental spectrum, the calculated spectra show two major vibrational bands at 2880 and 2940 cm⁻¹. The data presented in Table 2 shows that the

Table 2. Percentage Composition ⁴⁴ of the Main Vibrational
Bands of the Calculated Spectrum in the $(0^\circ, 0^\circ)$
Orientation for α -Pinene

C-H Stretching Mode Descriptions ^b						
$2880 \text{ cm}^{-1} \text{ band}$		2940 cm ⁻¹ band				
component	amount (%)	component	amount (%)			
η _ν χCH ₃ symm.	67	βCH_2 symm.	37			
$ ho CH_2$ symm.	5	$(CBFR)^d \beta CH_2$ symm.	40			
$ ho { m CH}_2$ antisymm.	12	$(OBFR)^d \eta_{\lambda} CH_3$ symm.	19			
$(CBFR)^{c} \rho CH_2$ symm.	4	νCH_3 asymm.	1			
$(CBFR)^c \eta_{\lambda} CH_3$ symm.	8					
other	4	other	3			

^{*a*}Percentage composition for a given mode within a band is calculated as the computed intensity the mode divided by the sum of modal intensities for the band. ^{*b*}Vibrational modes greater than 5% of the total for any band composition are listed. All other bands are specified in combination as "other". ^{*c*}CBFR = combination band Fermi resonance. ^{*d*}OBFR = overtone band Fermi resonance.

intensity of the 2880 cm⁻¹ band is dominated (ca. 67%) by a symmetric C–H stretching mode of the ^{η}CH₃ groups, while the ^{ρ}CH₂ symmetric and asymmetric C–H stretching modes account for most of the remaining intensity in the band. Other modes below 2900 cm⁻¹ account for less than 4% of the intensity of the 2880 cm⁻¹ band. For the 2940 cm⁻¹ band, the ^{β}CH₂ symmetric stretch is the source of ca. 77% of the intensity, and an overtone vibrational band of the ^{η}CH₃ symmetric stretch accounts for most of the remaining intensity (ca. 20%).

Repeating this analysis with calculated SFG spectra that did not account for Fermi resonances but instead only considered normal modes resulted in calculated spectra that are in significantly poorer agreement compared with the analysis that includes Fermi resonances. This result is shown in Figure 3 for the orientation corresponding to $(\theta, \psi) = (0^\circ, 0^\circ)$. At this orientation, neglecting Fermi resonances increased the normalized error by approximately 5-fold (0.26 compared with 0.056). The corresponding normalized error plot also shows a significant reduction in "blue" zones (regions of small error) and a concurrent increase in "red" zones (regions of large error, see Supporting Information Figure S1). We conclude that accounting for Fermi resonances is necessary for obtaining calculated SFG spectra that reproduce well the experimental SFG spectra of α -pinene.

III.B. Accounting for α -Pinene–Silica Interaction Dynamics Reveals Highly Fluxional Orientation Distributions. To evaluate the dynamics of the interactions between α -pinene and the fused silica surface, we applied classical



Figure 3. Normalized simulated vSFG spectra for Euler angles ($\theta = 0^\circ$, $\psi = 0^\circ$) with (red) and without (blue) accounting for Fermi resonance compared with the experimental spectrum (gray).

(CHARMM) MD simulations combined with DFT electronic structure calculations as described in the Methods section. We expect these interactions to be dominated by weak van der Waals forces, making it unlikely that a single orientation will be sufficient for proper modeling of the ensemble spectrum measured by experiment. As such, we developed a methodology for incorporating MD simulations to simulate a vSFG spectrum based on an ensemble of 130 α -pinene molecules. As a comparison, we also used the DFTB potential to simulate the dynamics of a *subsystem* (see Methods).

To probe the orientation of the α -pinene molecules, we defined an internal *z*-coordinate as shown in Figure 4A. Note



Figure 4. (A) The *z*-component of the green vector connecting the methylene and axial methyl carbon atoms is recorded for each α -pinene and monitored as a function of time. (B) Histogram of *z*-values for 130 α -pinene molecules over a 10 ns MD simulation.

that the choice of this coordinate is arbitrary and that any such coordinate defines the absolute orientation of the molecule, given the rigidity of α -pinene's bicyclic structure. The coordinate of our choice corresponds to the *z*-component of the vector connecting the ${}^{\beta}CH_2$ and ${}^{\chi}CH_3$ carbon atoms and is calculated for each snapshot. Its distribution is monitored as a function of time. The distribution is well converged after approximately 8 ns (see Supporting Information Figure S2). Therefore, we averaged the calculated spectra over a 10 ns classical MD simulation throughout this work. The internal *z*-coordinate distribution (Figure 4B) peaks at *z*-values of ca. +3.5 and -3.5 Å, corresponding to configurations with the $C-{}^{\chi}CH_3$ bond and the bisecting vector between the C-H bonds of the β -methylene group pointing away and toward the silica surface, respectively.

The *z*-coordinate versus time (z-t) profile for three selected α -pinene molecules reveals flipping between the "up" and "down" orientations (Figure 5) in a fashion that Fourier



Figure 5. The *z*-coordinate versus time profile for three selected α -pinene molecules from the classical MD simulation.

transforms indicate to be nonperiodic (data not shown). Global analysis of the z-t profiles indicates that approximately 27 (16) percent of the snapshots sampled from the MD simulations are in the "up" ("down") configurations. The histogram displayed in Figure 4B clearly shows that the bimodal molecular orientation distribution is biased heavily, by a ratio of almost 2:1, toward the "up" configuration. This result is robust over two independent trajectories that we ran and appears to be in good agreement with the orientation analysis obtained from the zero-interaction potential approach described in the previous section (namely, the orientations shown in Figure 2B,C). The highly fluxional interaction dynamics is also observed in a DFTB MD simulation of a single α -pinene molecule using a cluster model of silica (See Figure S3 in Supporting Information), albeit with different contributions of "up" vs "down" configurations. Further inspection of the histogram indicates that α -pinene molecules oriented with z-coordinate values between +2.5 and -2.5 Å show marked differences between the overall trajectory-averaged spectrum and the experimental spectrum. However, we find that the total intensity of the computed spectral responses produced by α -

To further quantify the rotationally fluid adsorption state of α -pinene on silica, we obtained the rotational reorientation time for the unit vector defined in Figure 4A. The ensembleaveraged reorientational autocorrelation function is shown in Figure 6. An optimal fit was provided by a double-exponential



Figure 6. Reorientational autocorrelation function for α -pinene molecules adsorbed on silica. The autocorrelation function is fitted with a double exponential (red dotted line) to obtain the rotational reorientation times of 2549 and 48 ps. The graph of a single exponential fit is provided in Figure S4 in the Supporting Information.

decay curve signifying two broad adsorption modes of α -pinene on silica, according to

$$C(t) = a_0 \left[\beta \exp\left(-\frac{t}{\tau_{\text{slow}}}\right) + (1-\beta) \exp\left(-\frac{t}{\tau_{\text{fast}}}\right) \right]$$
(9)

Here, $\tau_{\rm slow}$ and $\tau_{\rm fast}$ are reorientation times associated with two different modes of adsorption, and β is the pre-exponential factor providing the relative contributions of both time constants. Through this model, we obtained two reorientation times of 2580 ± 60 ps ($\tau_{\rm slow}$) and 49 ± 1 ps ($\tau_{\rm fast}$) with populations of about 47 ± 0.4% and 53 ± 0.4%, respectively. These reorientation times are in accord with the z-t profiles shown in Figure 5. As noted in Figure 4B, the populations of "up" and "down" versus other configurations (*z*-values between +2.5 and -2.5 Å) are approximately 43% and 57%, respectively. In light of the similarity between the two ratios, we attribute the longer reorientation time to α -pinene molecules in the "up" or "down" configurations, which are more tightly bound.

Furthermore, it is known that ultrafast orientational motions with large amplitude may cause SFG signal cancellations in specific polarizations (i.e., sps polarization combination).^{87–90} However, such effect was usually too small even for small water molecules on the air/water interfaces.^{87,88} The α -pinene reorientational dynamics here is also much slower to have such effect. In addition, such motion effect on the SFG spectra is essentially negligible in the ssp polarization combination.

III.C. The Bridge Methylene Group on the Four-Membered Ring (" $^{\mu\beta}CH_2$ ") of α -Pinene Is Estimated To Produce 70–80% of the Dominant Spectral Feature in the SFG Spectrum. Figure 7 demonstrates good agreement between the experimentally measured (black) and calculated



Figure 7. Comparison of the calculated ensemble-averaged SFG spectrum (red trace) with the experimental SFG spectrum of α -pinene (black trace) in contact with a fused silica surface.

ensemble-averaged (red) spectra of α -pinene molecules interacting with the fused silica surface studied here. The calculated ensemble-averaged spectrum is also in good agreement with the spectrum obtained from the zerointeraction potential approach described in the previous section (Figure 2D). Table 3 lists the compositions of the major

Table 3. Percentage Composition for Main Vibrational Bands of Calculated Ensemble-Averaged Spectrum of α -Pinene from MD Simulations

C–H Stretching Mode Description ^a						
2880 cm ⁻¹ band		2940 cm ⁻¹ band				
component	amount (%)	component	amount (%)			
η_{λ} CH ₃ symm.	74	βCH_2 symm.	37			
$ ho CH_2$ symm.	6	$(CBFR)^{b} \beta CH_{2}$ symm.	42			
$ ho { m CH}_2$ antisymm.	12	$(OBFR)^b \eta_{\chi} CH_3$ symm.	12			
$(CBFR)^{b} \rho CH_{2}$ symm.	3	$\eta_{\eta} \chi CH_3$ asymm.	3			
$(CBFR)^b \eta_{\lambda} CH_3$ symm.	1	νCH_3 asymm.	1			
νCH_3 symm.	2	bridging CH (ν)	3			
		bridging CH (ρ)	1			
other	2	other	1			

^{*a*}Vibrational modes with greater than 5% of the total contribution for any band composition are listed. All other bands are specified in combination as "other". ^{*b*}CBFR = combination band Fermi resonance. ^{*c*}OBFR = overtone band Fermi resonance.

vibrational bands for the ensemble-averaged calculated spectrum. These values are in good agreement with the vibrational band compositions obtained using the zero-interaction potential approach (Table 2). The dominant contributions to the 2880 cm⁻¹ band are from the symmetric C–H stretching modes of the ^{η_{α}}CH₃ groups and the ^{ρ}CH₂ group, accounting for ca. 74% and 18%, respectively. The vinyl ^{ν}CH₃ symmetric stretching mode plays a somewhat larger role (ca. 2%) in the 2880 cm⁻¹ band of the ensemble-averaged spectrum, which is likely due to the sampling of orientations where the ^{ν}CH₃ dipole derivative magnitude has a greater



Figure 8. Lowest energy ONIOM(ω B97XD/6-31G(d):HF/3-21G) optimized geometries of a cluster model of fused silica with snapshots sampled from DFTB MD simulations. (A) lowest energy orientation (z = 3.0 Å); (B) second lowest energy orientation (relative energy +0.74 kcal mol⁻¹ and z = -0.64 Å); (C) third lowest energy orientation (relative energy +1.24 kcal mol⁻¹); (D) fourth lowest energy orientation (relative energy +1.59 kcal mol⁻¹).

projection onto the *yyz* tensor element of the $\chi^{(2)}$ tensor. All other modes account for less than 5% of all bands found below 2900 cm⁻¹. Above 2900 cm⁻¹, the ensemble-averaged spectrum shows that the 2940 cm⁻¹ band is composed ca. 79% by the ${}^{\beta}$ CH₂ stretch, in good agreement with the results obtained from the zero-interaction potential approach. An overtone band in Fermi resonance with a symmetric C–H stretching mode for the ${}^{\eta_{\mathcal{X}}}$ CH₃ groups contributes ca. 12% to the 2940 cm⁻¹ band intensity in the ensemble averaged spectrum. Finally, two bridging CH stretching modes account for ca. 3% of the 2940 cm⁻¹ band due to the greater sampling of orientations away from (0°, 0°) compared with the zero-interaction potential approach.

To provide more accurate estimates of the interaction energies with the silica surface at different orientations, we further carried out two-layer ONIOM (ω B97XD/6-31G-(d):HF/3-21G) geometry optimizations on a cluster model of fused silica using snapshots randomly sampled from DFTB MD simulations. The ω B97X-D functional⁹¹ was chosen, because it includes empirical corrections for dispersion, which is likely to be important. The lowest energy orientations and their relative energies obtained from this analysis are shown in Figure 8. Notably, there is no large energy difference between the various orientations sampled from the MD simulations, and their energies are generally within 1-2 kcal mol⁻¹. Since an energy difference of 1.4 kcal mol⁻¹ corresponds to an order of magnitude difference in population at room temperature, these energies are in qualitative accord with the molecular orientation distribution extracted from the classical MD simulations (Figure 4B). The orientation corresponding to z = +3.0 Å is

lowest in energy presumably because this particular orientation provides the largest van der Waals contact between the α pinene molecule and the silica surface. We conclude from the results presented in this section that the α -pinene-silica interaction dynamics are highly fluxional and sample a bimodal orientation distribution whose two most probable orientations are "up" and "down" with respect to the bridge methylene group. MD simulations based on a more accurate potential (e.g., QM/MM) to quantify which population dominates are ongoing, as are experiments aimed at determining the absolute net orientation of the bridge methylene group over α -quartz.

The finding of rotationally fluid dynamics by MD at room temperature suggests that the surface-bound α -pinene molecules may be energetically stabilized by rotational entropy. We calculated the gain in rotational entropy (\overline{S}_{rot}^{ads}) relative to the static state using statistical mechanics, as described by Behm and co-workers,⁹² and DFT-optimized atomic coordinates of gas phase α -pinene. Through this analysis, we obtain an entropic stabilization energy, $T\overline{S}_{rot}^{ads}$, of ~11 kJ/mol at 300 K, which is comparable to that obtained for methyl-butyl-thioether in Behm's work. Here, however, we show stabilization due to rotational entropy gains for a molecule without heteroatoms. Ongoing work will utilize DFTB MD to calculate entropic stabilization, explicitly accounting for α -pinene–SiO₂ interactions.

IV. CONCLUSIONS

We have studied the C–H stretching modes responsible for the vSFG spectrum of α -pinene adsorbed on fused silica using a combination of theoretical techniques and direct comparisons

to experimental data. Accounting for Fermi resonances was shown to improve the description of the SFG responses. With or without taking the fluxional dynamics identified here into account, we find from static DFT calculations that the 2940 cm⁻¹ peak corresponding to the largest SFG signal intensity in the spectrum is largely (ca. 77-79%) due to the ${}^{\beta}CH_{2}$ symmetric stretch and Fermi resonance, with the remainder of the intensity being largely due to an overtone vibrational band of the $^{\eta\chi}$ CH₃ symmetric stretch. The intensity of the 2880 cm⁻¹ band is dominated (ca. 67–74%) by a symmetric C-H stretching mode of the $^{\eta,\chi}$ CH₃ groups, while the $^{\rho}$ CH₂ symmetric and asymmetric C-H stretching modes account for most of the remaining intensity in that band. The vinyl ^{*v*}CH₃ symmetric stretching mode plays a somewhat larger role (ca. 2%) in the 2880 cm^{-1} band of the ensemble-averaged spectrum as opposed to the static calculations. This outcome is likely due to the importance of dynamics in which the ^vCH₃ dipole derivative magnitude has a greater projection onto the yyz tensor element of the $\chi^{(2)}$ tensor than what is sampled in the static DFT calculations.

Our results suggest that α -pinene is oriented on average such that its $C - \chi CH_3$ bond is nearly orthogonal to the surface plane. Hybrid ONIOM calculations on snapshots sampled from DFTB molecular dynamics simulations indicate that such a preferred orientation gives rise to the largest van der Waals contact with the silica surface. Accounting for α -pinene-silica interaction dynamics reveals a highly fluxional and bimodal orientation population that is characterized by "up" vs "down" orientations of the $C-\chi CH_3$ bond. Given that the axial (" χ CH₃") and the vinyl (" ν CH₃") methyl groups point toward the surface when the $C-\chi CH_3$ bond points down, we expect that particular "down" orientation to allow for reaction with the π -electrons of the C=C double bond, since they are now readily accessible for incoming reactants. The "up" orientation of the $C-\chi CH_3$ bond would lead to substantial steric hindrance by the axial (" $^{\chi}CH_3$ ") and the vinyl (" $^{\nu}CH_3$ ") methyl groups that now point toward the gas phase. While it is not yet known from our experiments which populations dominates, the implications of our finding of a highly fluxional surface state of α -pinene, under the conditions of our study, are that (1) the rotational entropy penalty for adsorption from the gas phase is unlikely to be high, (2) heterogeneous oxidation of the C=Cdouble bond is likely to be facile for the "down" orientation of the C- χ CH₃ bond, and (3) α -pinene adsorbed to surfaces other than SiO₂, including those formed at the organic aerosol particle/gas boundary or at catalyst/feedstock boundaries, may be subject to fluxional orientation dynamics as well. This last finding will be particularly important for improving catalytic routes in the heterogeneous transformations of α -pinene, a potentially sustainable feedstock for fine chemicals and polymers.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b03158.

Force field parameters for classical MD simulations, contour plot of the normalized error between the pure harmonic and experimental spectra, convergence of *z*-histograms of pinene molecules from MD simulations at different simulation times, and *z*-histogram from DFTB

trajectory of a pinene molecule on a cluster model of fused silica (PDF)

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Notes

The authors declare no competing financial interest.

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