Vibrational Mode Assignment of α-Pinene by Isotope Editing: One Down, Seventy-One To Go

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Ⓢ Supporting Information

ABSTRACT: This study aims to reliably assign the vibrational sum frequency generation (SFG) spectrum of α-pinene at the vapor/solid interface using a method involving deuteration of various methyl groups. The synthesis of five deuterated isotopologues of α-pinene is presented to determine the impact that removing contributions from methyl group C−H oscillators has on its SFG response. 0.6 cm^{-1} resolution SFG spectra of these isotopologues show varying degrees of differences in the C−H stretching region when compared to the SFG response of unlabeled α-pinene. The largest spectral changes were observed for the isotopologue containing a fully deuterated vinyl methyl group. Noticeable losses in signal intensities allow us to reliably assign the 2860 cm^{-1} peak to the vinyl methyl symmetric stretch. Furthermore, upon removing the vinyl methyl group entirely by synthesizing apopinene, the steric influence of the unlabeled C_9H_{14} fragment on the SFG response of α-pinene SFG can be readily observed. The work presented here brings us one step closer to understanding the vibrational spectroscopy of α-pinene.
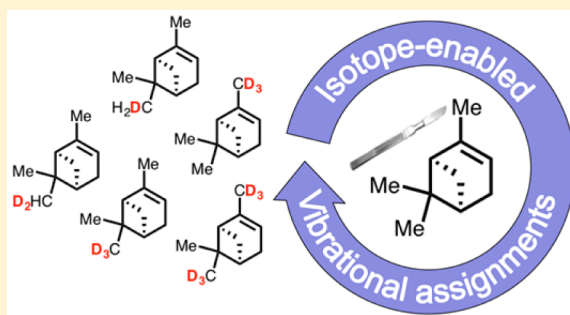
1. INTRODUCTION

Naturally occurring terpenes such as α-pinene serve as important intermediates in fuel production, are valuable chemical feedstocks for synthetic polymers and pharmaceuticals, and are major contributors to atmospheric aerosol formation.[1−13] Many of the critical processes involving these hydrocarbons and their oxygenated derivatives occur at condensed matter interfaces, as well as solid/gas interfaces, and are believed to be sensitive to molecular structure, conformation, and orientation distributions.[13−24] Unfortunately, the acquisition of structural data for these species within interfacial environments remains challenging. Second-order nonlinear vibrational spectroscopies are generally bond-specific and can be configured to be surface-selective and submonolayer sensitive, making them potentially ideal tools for investigating processes involving terpenes at catalytically or environmentally relevant interfaces.[25−28] However, due to limited spectral resolution or complicated and overlapping spectral line shapes (every C−H oscillator should contribute to the spectral response), their vibrational assignments in the C−H region are usually unreliable. For instance, though Wilson's classic paper on the infrared and Raman spectra of α-pinene states that "all 72 modes of vibration are allowed in both the infrared and Raman",[29] assignments given in the literature for this molecule in the C−H region, and many others like it, remain at best approximate. As a consequence, the mechanistic information needed to understand, control, and predict how

small hydrocarbons behave within interfacial environments remains elusive.

Nonlinear optical spectroscopy holds the promise of enabling a bond-specific and molecular level understanding of chemistry and structure of condensed matter at solid/gas interfaces. Vibrational sum frequency generation (SFG) spectra[30−34] in particular have provided important molecular information regarding the structure of hydrocarbons at surfaces and interfaces, yet many systems studied by SFG remain complex and poorly understood. Fortunately, recent advances in high-resolution vibrational SFG have made it possible to investigate systems with a level of molecular detail and reliability that cannot be achieved with conventional SFG spectroscopy.[35−38] In addition, the simulation of SFG spectra of small hydrocarbons through atomistic calculations has progressed to the point where their reliability can be validated through the use of isotope labeling.[39,40] These developments have allowed us to take the next step toward a reliable vibrational assignment of the SFG spectrum of α-pinene, a highly abundant and naturally occurring terpene,[5,41] at the vapor−solid interface. Our work builds upon our recently reported sub-1 cm^{-1} resolution SFG spectrum of unlabeled α-pinene that provided accurate line shapes, allowing us to identify vibrational modes near 2923 and

2930 cm^{-1} with vibrational decoherence lifetimes of 1.4 and 1.7 ps, respectively.[36] The Lorentzian fitting method used in that approach is frequently applied for assigning vibrational modes to determine interfacial structure and molecular orientation distributions.[38,42]

Direct mode assignments are possible through isotope labeling, which can also be used to test tentative assignments obtained from peak fitting. Given the coherent nature of SFG spectroscopy, isotope labeling enables us to observe intensity changes in vibrational spectra of isotopologues upon deuteration of specific C−H oscillators. We emphasize the use of the word "change", as opposed to "disappear", as the observed SFG intensity is due to the coherent superposition of the E-fields produced by the SFG-active oscillators at a given vibrational frequency and those coupled to vibrational modes oscillating at nearby frequencies. The feasibility of this approach has been demonstrated previously in the analysis of the SFG spectrum of trans-β-isoprene epoxydiol, an important atmospheric aerosol particle constituent.[39] Here, we synthesize five deuterium-labeled isotopologues of α-pinene as well as a simplified α-pinene derivative (Figure 1) so as to determine the
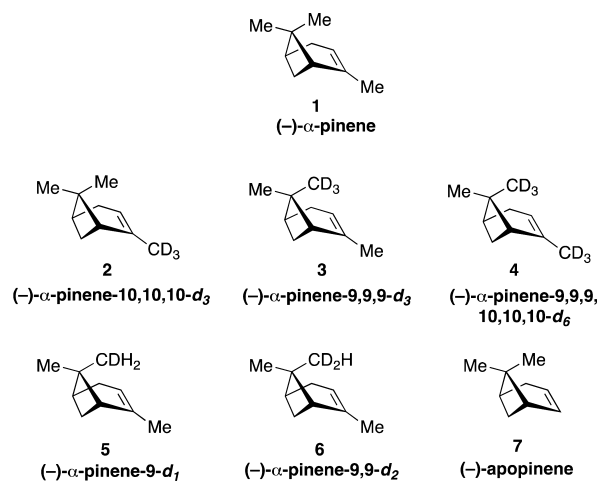

**Figure 1.** Synthetic α-pinene isotopologues and derivatives analyzed in this study.

impact of removing contributions from various C−H oscillators on the SFG response of α-pinene. Our results enable us to unambiguously make two vibrational mode assignments that bring us one step closer to understanding the complex vibrational spectrum of α-pinene.[29] Future work will use vibrational mode assignments of α-pinene to help identify surface oscillators in α-pinene-derived aerosols, which have similar surface SFG spectra.

2. EXPERIMENTAL SECTION

2.1. Synthesis of α-Pinene Isotopologues Containing Deuterated Vinyl and/or Endo Methyl Substituents and α-Pinene Derivative Apopinene. Our initial attempts to access (−)-α-pinene-10,10,10-d_3 (**2**) involved following the route developed by Skattebol and co-workers,[43] where **2** was synthesized through the ozonolysis of β-pinene (**8**) followed by treatment with a deuterated methyl Grignard reagent and a final elimination to yield the desired product. However, this method resulted in both low yields and the consistent contamination of the desired deuterated α-pinene compound with β-pinene. To circumvent these issues, we devised an alternative route to

access (−)-α-pinene-10,10,10-d_3 (**2**), as shown in Scheme 1. Ozonolysis of β-pinene (**8**) to afford nopinone (**9**) proceeded

Scheme 1. Synthesis of α-Pinene Isotopologues 2−6
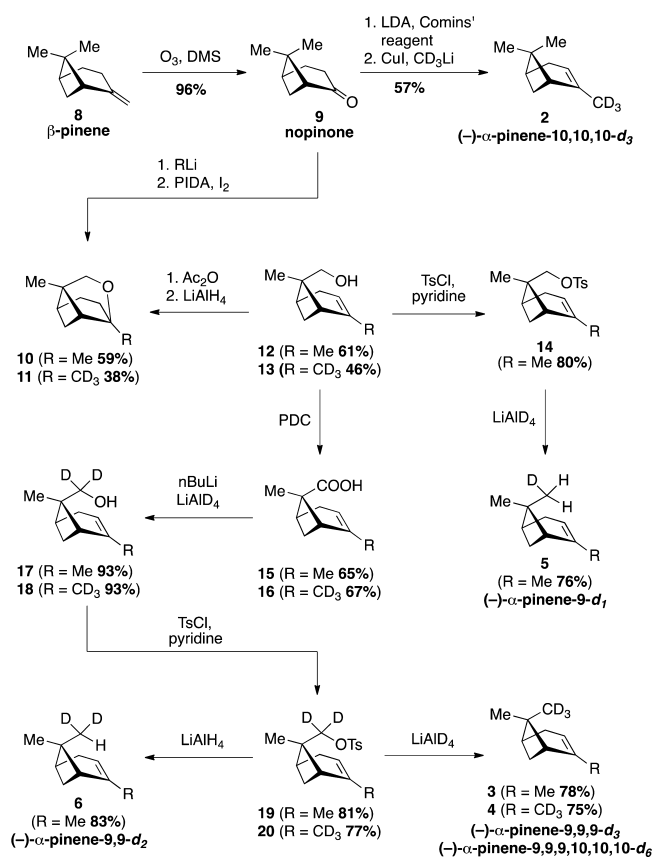
in 96% yield on a 40 g scale. Treatment of ketone **9** with LDA and trapping with Comins' reagent gave the enol triflate, which underwent subsequent copper-mediated coupling with deuterated methyllithium to afford (−)-α-pinene-10,10,10-d_3 (**2**) in 57% yield over two steps from ketone **9**.[44] This route enabled ready access multigram quantities of (−)-α-pinene-10,10,10-d_3 (**2**) free from contamination by β-pinene (**8**).

After developing a synthesis for isotopologue **2**, we set out to obtain the more synthetically challenging endo methyl labeled α-pinene (i.e., **3**). Borden and co-workers had previously labeled the endo methyl group of α-pinene beginning with the treatment of **9** with methyllithium to produce the desired alcohol with relatively low conversion, presumably due to competing enolate formation.[45] Under the same conditions, we observed similar results (60% conversion to the desired alcohol), whereas attempts to use the Grignard reagent or add CeCl$_3$ to promote the 1,2-addition[46,47] over the competing enolization were unfruitful. Nevertheless, sufficient quantities of the desired alcohol were obtained and we proceeded with the selective C−H functionalization of the endo methyl substituent. Borden and co-workers originally accomplished this transformation using mercuric oxide and bromine to give the caged ether **10**.[45] In an attempt to circumvent the need for stoichiometric mercury, we investigated conditions developed by Suárez and co-workers for related transformations.[48] Thus, we treated the alcohol product with PIDA and I$_2$, in the presence of illumination by a tungsten lamp. Under these conditions, the tertiary alcohol product underwent C−H

functionalization to afford caged ether **10** in 59% yield over the two steps.

The caged ether was subsequently opened with acetic anhydride and the resulting acetate removed with $LiAlH_4$ to give alcohol **12** in 61% yield over the two steps. Oxidation of alcohol **12** to carboxylic acid **15** with PDC proceeded with low conversions, giving a 1:1 ratio of aldehyde to acid. After two consecutive purifications and resubmissions to the reaction conditions, acid **15** was obtained in an overall yield of 65%. Attempts to improve the yield with either a Pinnick or Corey−Gilman−Ganem oxidation[49] resulted in no desired product. Deprotonation of the carboxylic acid **15** with *n*BuLi followed by reduction with $LiAlD_4$ afforded the desired alcohol **17** in 93% yield.

Tosylation of the resulting alcohol, followed by displacement with $LiAlD_4$ gave the desired (−)-α-pinene-9,9,9-d_3 **3** in 64% yield over the two steps. Although the original synthesis published by Borden and co-workers[45] suggested the use of Super-Deuteride in the final step, we found that $LiAlD_4$ accomplished this transformation in just 30 min at room temperature. The synthesis was also carried out starting with deuterated methyl lithium addition to **9** to ultimately afford (−)-α-pinene-9,9,9,10,10,10-d_6 (**4**) with comparable yields. To further analyze the contributions of the endo methyl group to the vibrational spectrum of α-pinene, isotopologues **5** and **6** were prepared in an analogous fashion to **3** as indicated in Scheme 1.

Apopinene (**7**) maintains the bicyclo[3.1.1]heptene core of α-pinene but lacks the vinylic methyl substituent. Apopinene (**7**) can be readily synthesized in one step from myrtenal, a common ingredient in food flavoring and therefore relatively abundant terpene, through a palladium-mediated decarbonylation.[4]

2.2. Sum Frequency Generation (SFG) Spectroscopy and Sample Cells. The standard resolution SFG laser system used here has been previously described.[27,50,51] Briefly, a Ti:S femtosecond laser system operating at 1 kHz repetition rate (Spectra Physics, Spitfire Pro) is used. Half of the 800 nm output is used to pump an optical parametric amplifier (Spectra Physics, OPA 800C) to generate a tunable broadband IR beam covering the aromatic and aliphatic C−H stretching region. A visible pump beam is used to upconvert the IR light field at the sample surface, giving an 800 nm pump pulse with a bandwidth of 1.57 nm. The incident pulse energies and foci are limited to 2 μJ and 50 μm in diameter, respectively, to avoid any optical damage.

Internal reflection geometries are employed in all experiments, as well as the *ssp* polarization combination, which probes the components of the vibrational transition dipole moments that are oriented perpendicular to either SiO_2 or CaF_2 substrates. The substrates were chosen because of their optical properties and to test how important the presence of surface hydroxyl groups is for the SFG responses of α-pinene. Spectra shown in this work are averages of the individual experiments repeated several times, and high-resolution spectra were normalized to the highest peak intensity. In the case of the standard resolution system, spectra were collected for 7 acquisitions, lasting 2 min, and were referenced to the SFG response from a gold substrate to account for energy variations in the IR pulse. Frequencies are also calibrated using a polystyrene standard (ICL Crystal Laboratories).

The high-resolution SFG laser system has been described previously[35,36] and differs from the standard resolution system

in that it utilizes short (<40 fs high resolution vs ∼100 fs standard resolution) IR pulses that are overlapped with long duration (∼90 ps high resolution vs ∼2 ps standard resolution) visible pulses. The duration of the visible pulse prevents spectral broadening, enabling us to collect spectra with 0.6 cm^{-1} resolution using a 750 mm focal length spectrograph and CCD camera. The use of high-resolution SFG allows us to resolve several peaks that appear as only shoulders or are unresolved in the broadband SFG spectra. For reference, the standard resolution broadband SFG system described in this work provides approximately 10 cm^{-1} resolution. The energies of the visible and IR pulses are ∼300 μJ and ∼28 μJ, respectively. Three 10 min sample and 10 min background scans were collected and normalized to z-cut quartz for each spectrum.

The compounds under investigation were analyzed at room temperature using SFG by contacting either a fused silica or CaF_2 window with their equilibrium vapor pressure. In these experiments, approximately 30 μL of sample was injected through a syringe into the open space of a custom-built Teflon sample cell containing an opening against which an optical window is sealed using an O-ring. After a given compound was introduced into the cell, the vapor was allowed to equilibrate such that the incident laser fields did not illuminate the condensed phase of the compounds studied.

3. RESULTS AND DISCUSSION

3.1. SFG Spectra of α-Pinene Isotopologues Containing Deuterated Vinyl and/or Endo Methyl Substituents.

The standard resolution SFG spectra of the deuterated α-pinene analogues each display lower overall intensity (Figure 2) when compared to the spectra of unlabeled species. This result
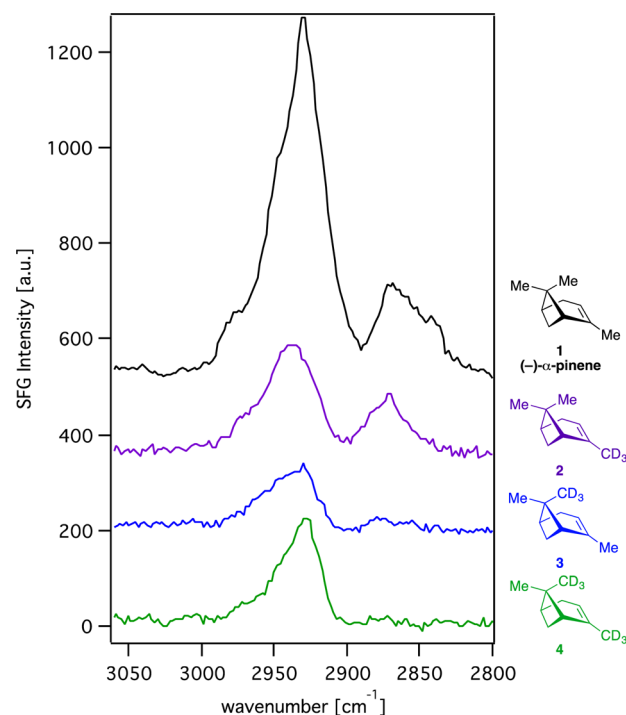

Figure 2. Standard resolution broadband SFG spectra (−)-α-pinene (**1**, black) and α-pinene isotopologues **2** (purple), **3** (blue), and **4** (green) as vapor phases in contact with fused silica. Spectra are offset for clarity.

is expected, given the general dependence of the SFG intensity on the number of oscillators. In addition, we note changes in the relative intensities of the peaks when compared to spectra of unlabeled α-pinene. Although these changes may provide some insight into how specific oscillators contribute to the SFG signal, the spectra remain congested, and deconvoluting the spectral contributions is difficult. Not surprisingly, the high-resolution SFG spectra of the deuterated α-pinene analogues collected at Pacific Northwest National Laboratory (PNNL) (Figure 3) exhibit more clearly resolved spectral features when
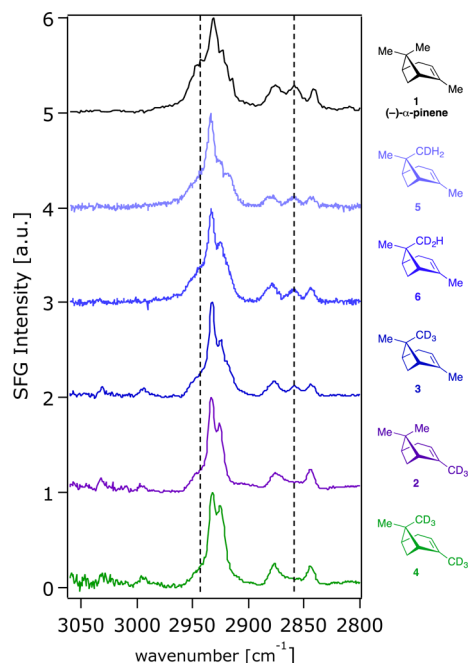

Figure 3. 0.6 cm^{-1} resolution SFG spectra of $(-)$-α-pinene (**1**) and α-pinene analogues (**2**−**6**) as vapor phases in contact with CaF$_2$. Spectra are offset and normalized to the highest intensity peak for clarity. Dashed lines indicate peak positions at 2940 and 2860 cm^{-1}.

compared to the standard resolution spectra and decreased signal intensity when compared to spectra of the unlabeled species. Moreover, the high-resolution SFG spectra collected on CaF$_2$ (Figure 3) and fused silica (Figure S1) are spectrally similar, indicating little influence of surface hydroxyl groups on the SFG responses of α-pinene.

The high-resolution SFG spectra of α-pinene vapor at the CaF$_2$ interface show three well-resolved resolved peaks below 2900 cm^{-1}. Stepwise deuteration of the endo methyl group (isotopologues **5**, **6**, and **3**) only negligibly impacts the SFG response. In contrast, the intensity of the peak centered at 2860 cm^{-1} decreases almost entirely when the vinyl methyl group of α-pinene is deuterated in isotopologues **2** and **4**. Vapor phase IR spectra of α-pinene compared to spectra of isotopologue **2** show similar decreases in signal intensity at 2860 cm^{-1} (Figure S2). Overall, the SFG spectra of α-pinene and the deuterated isotopologue **2** appear simplified relative to their corresponding absorbance spectra. This result may be due to polarization selections and orientation effects as well as changes in Fermi resonance contributions.

There are also SFG intensity differences at 2940 cm^{-1} that coincide with deuteration of the vinyl methyl and the endo methyl group in isotopologues **2**, **3**, and **4**. This effect is less pronounced on the fused silica substrate (Figure S1) than on

the CaF$_2$ substrate and is not observed in the vapor phase IR spectrum of isotopologue **2** (Figure S2). This spectral feature cannot be resolved, even with the 0.6 cm^{-1} resolution SFG spectrometer. Other small differences in the spectrum are noted as well, including slightly better resolution of the shoulder of the main peak. This shoulder peak at 2920 cm^{-1} also appears to change upon deuteration of the vinyl methyl group (**2**) and may contain contributions from the asymmetric methyl stretching mode but is difficult to unambiguously assign. Finally, isotopologues **2**, **3**, and **4** show minor signal contributions near 3000 cm^{-1}, possibly indicating contributions from the vinyl C−H oscillator.[52] Deuteration of the endo and vinyl methyl groups does not appear to alter the SFG responses at other frequencies, indicating that these resonances originate from the other C−H oscillators in α-pinene that have not yet been deuterated.

The loss of spectral intensity at 2860 cm^{-1}, which coincides with deuterating the vinyl methyl group, allows us to unambiguously assign these frequencies to the symmetric stretch of the vinyl methyl group. The lower than expected frequency of this mode relative to the methyl groups present on the four membered ring may be due to a combination of the strain in the bicyclic system of α-pinene as well as coupling between the bridge methyl groups and Fermi resonance contributions. We note that deuterium labeling of both the endo and vinyl methyl groups together (isotopologue **4**) produces the same SFG response we obtained for the vinyl isotopologue **2**, whereas the endo isotopologue **3** produces an SFG response more similar to that of the unlabeled species **1**. This result indicates that the endo methyl group does not contribute significantly to the SFG response of the species surveyed, which is consistent with the notion that this group is oriented away from the direction of transition dipole moment elements probed by the *ssp* polarization combination, i.e., that it is oriented parallel to the surface. Having identified the vinyl symmetric stretching mode at 2860 cm^{-1}, we attempted to determine an orientation distribution for the symmetric stretching mode by comparing signal intensities from *ssp* and *ppp* polarization combinations, where the *ppp* polarization combination probes oscillators oriented parallel to the surface. Unfortunately, low *ppp*-polarized SFG signal intensity at 2860 cm^{-1} prevented us from doing so. Future efforts will focus on the use of methods such as the polarization null angle (PNA) method to reliably determine orientations of modes where lower *ppp* signal intensities are observed.

3.2. SFG Spectra of Apopinene. In general, the isotope labeling strategy outlined above is ideal for effectively removing contributions from C−H oscillators without dramatically changing the steric properties of the molecule. By comparing $(-)$-α-pinene isotopologue **2**, where the vinyl methyl group is fully deuterated, and $(-)$-apopinene (**7**), where the vinyl methyl group is missing entirely, one should readily observe the steric influence of the unlabeled C$_9$H$_{14}$ fragment on the SFG response of α-pinene. In addition to our interest in the fundamental spectroscopic properties of apopinene, this molecule has also been shown to be a biorenewable monomer for preparing polymers,[4] warranting spectroscopic analysis. We therefore set out to synthesize this molecule and to probe it using vibrational SFG spectroscopy.

Figure 4 compares the high-resolution SFG spectrum of apopinene (**7**) with the spectra obtained from $(-)$-α-pinene and isotopologue **2**, all on CaF$_2$ substrates. Similar spectra collected on fused silica can be found in Figure S3. Figure 4
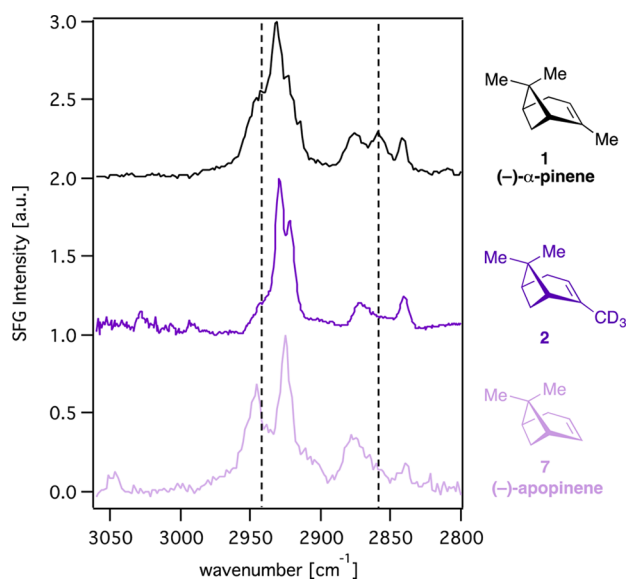
Figure 4. 0.6 cm^{-1} resolution SFG spectra of (−)-α-pinene (**1**), isotopologue **2**, and (−)-apopinene (**7**) as vapor phases in contact with CaF$_2$. Spectra are offset and normalized to the highest intensity peak for clarity. Dashed lines indicate peak positions at 2940 and 2860 cm^{-1}.

demonstrates that complete removal of the vinyl methyl group of α-pinene in the case of apopinene (**7**) results in a markedly different vibrational SFG spectrum when compared to the spectra obtained from the unlabeled α-pinene and isotopologue **2**: rather than the sharp peak observed at 2930 cm^{-1} in the spectra of unlabeled α-pinene and isotopologue **2**, separate peaks around 2945 and 2925 cm^{-1} are observed for apopinene (**7**). The SFG spectrum of apopinene (**7**) also shows a peak in the vinylic C−H stretching region at 3050 cm^{-1}. On the basis of our prior work on cyclic olefins tethered to fused silica substrates,[53] we attribute this outcome to the asymmetric H—C≡C—H nonlocal normal mode, whereas the symmetric stretch of this mode, located at 3000 cm^{-1}, appears to be of weak intensity.

The two peaks observed near 2945 and 2925 cm^{-1} for apopinene (**7**) indicate that the removal of the vinylic methyl group may significantly change the orientation of α-pinene at the vapor/solid interface and/or alter interferences with C−H oscillators that directly contribute to the high-intensity peak observed for α-pinene at 2930 cm^{-1}. In addition, the SFG spectrum of apopinene (**7**) shows a reduction in signal intensity for the center of the three peaks below 2900 cm^{-1}, similar to the spectra of isotopologues **2** and **4** containing deuterated vinyl methyl groups.

The data shown in Figure 3 indicate that using derivatives as opposed to isotopologues for elucidating complex vibrational spectra of rigid hydrocarbons is not feasible as differences in steric hindrance may be exogenous contributors to the SFG responses. In contrast, the selective synthesis of deuterated isotopologues effectively removes vibrational contributions from certain C−H oscillators while safely allowing for an assumption of invariant steric influences. However, due to the limited amount of SFG data available for complex hydrocarbons like terpenes, it is still useful to construct a library of spectra including compounds such as apopinene (**7**) for use in future analyses.

4. CONCLUSIONS AND FUTURE DIRECTIONS

Through a combined synthetic and spectroscopic approach utilizing isotopically labeled compounds, we have made progress in our attempt to better understand the vibrational spectroscopy of terpenes such as α-pinene. We have demonstrated that this method is useful for reliably assigning peaks in the *ssp*-polarized SFG spectrum of α-pinene at gas−solid interfaces. As mentioned in the Introduction, Wilson's classic paper on the infrared and Raman spectra of α-pinene highlights the fact that "all 72 modes of vibration are allowed in both the infrared and Raman".[29] Although we have successfully used selective deuteration to unambiguously assign one vibrational mode, and to specifically pinpoint which of the three methyl groups it belongs to, we are still faced with challenge of assigning the other important spectral features. More specifically, our future work will aim to assign the major signal intensity between 2930 and 2950 cm^{-1} in the surface vibrational spectrum of α-pinene, because a similar surface SFG intensity is also observed in atmospheric aerosol material derived from α-pinene. Therefore, assignment of this spectral feature in the C−H region as well as expansion of these SFG studies to the C≡O and C−D stretching region may lead to important insight into the surface-active oxidation products of aerosol material.

Though infrared and Raman spectroscopies are not particularly sensitive for determining spectral differences in compounds that differ in just two or three hydrogen vs deuterium atoms (viz. Supporting Information Figure S2), SFG spectroscopy is demonstrated here to be quite sensitive and up to the task. As such, we consider the method of applying SFG spectroscopy to isotopologues promising for assigning the vibrational modes of small hydrocarbons relevant to a variety of topics in environmental, materials, catalytic, and biological chemistry. A specific example of where we see this method going particularly far is in improving the limited understanding of the spectra of catalytically relevant hydrocarbons at metal surfaces,[54−57] whose SFG assignments remain largely empirical and have not been assessed in terms of reliability by methods such as deuteration.

Theoretical SFG simulations will direct future synthetic efforts toward targeting C−H oscillators that are predominantly responsible for the major signal intensity between 2930 and 2950 cm^{-1} in the surface vibrational spectrum of α-pinene. As previously mentioned, these assignments of α-pinene and the generation of α-pinene isotopologues will be particularly useful in our ongoing investigations of exchanges between the gas and aerosol phases of α-pinene-derived secondary organic aerosol material.[58−61]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b01995.

General synthetic methods, experimental procedures for the synthesis of α-pinene derivatives, supplemental SFG and IR spectra, ^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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