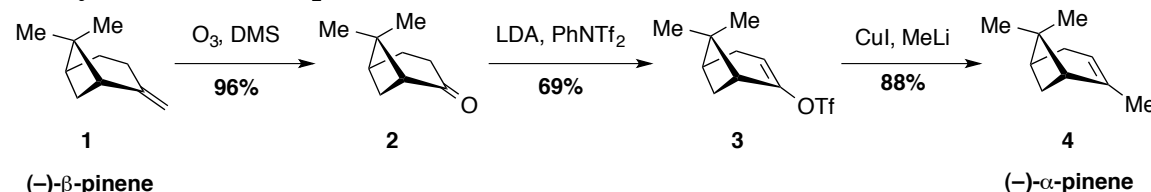


Supplementary Information for

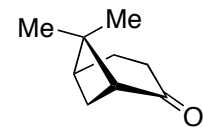
Accurate Lineshapes from Sub-1 cm⁻¹ Resolution Sum Frequency Generation VibrationalSpectroscopy of α -Pinene at Room Temperature

Amanda L. Mifflin^{1,†} Luis Velarde,^{2,†,‡} Junming Ho,³ Brian T. Psciuk,³ Christian F. A. Negre,³
 Carlena J. Ebben,^{4,#} Mary Alice Upshur,⁴ Zhou Lu,^{2,¶} Benjamin L. Strick,⁴ Regan J. Thomson,⁴
 Victor S. Batista,³ Hong-Fei Wang,^{2,*} and Franz M. Geiger^{4,*}

¹ Department of Chemistry, University of Puget Sound, Tacoma, WA 98416; ² William R. Wiley Environmental Molecular Sciences Laboratory Pacific Northwest National Laboratory, Richland, WA 99352; ³ Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107; ⁴ Department of Chemistry, Northwestern University, Evanston, IL 60208.

S1. Synthesis of (–)- α -pinene

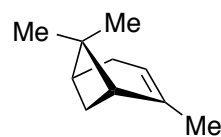
Scheme S1. Synthesis of (–)- α -pinene by a copper-mediated coupling with enol triflate.¹

 **(1R)-6,6-Dimethylbicyclo[3.1.1]heptan-2-one (2):** Ozone was bubbled through a solution of (–)- β -pinene (40 g, 294 mmol) in methanol (70 mL) at -78 °C. After 3 hours, O₂ was bubbled through for an additional 30 minutes. After addition of dimethyl sulfide (37 mL, 504 mmol) mixture was then allowed to warm to room temperature and stirred for an additional 12 hours. Reaction was transferred to a separatory funnel and diluted with CH₂Cl₂ (100 mL) and H₂O (100 mL). The organic phase was collected and aqueous layer extracted with CH₂Cl₂ (2 x 100 mL). The combined organics were washed with brine and dried using Na₂SO₄. Concentration under reduced pressure affording an oil. Flash column chromatography on silica gel using 5% EtOAc in hexanes as the eluent afforded the title compound as a clear oil. (39.0 g, 282 mmol, 96% yield): 97:3 e.r. [α]_D²⁰ = +20.7 (c 2.9, CHCl₃); IR (film) 2951, 1710, 1460, 1200, 1030 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 2.58–2.51 (m, 3H); 2.34 (ddd, 1H, J = 19.1, 9.2, 2.0 Hz); 2.25 (m, 1H); 2.05 (m, 1H); 1.94 (m, 1H); 1.58 (d, 1H, J = 10.4 Hz); 1.33 (s, 3H); 0.85 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 215.1,

1. McMurry, J. E.; Scott, W. J. *Tetrahedron. Lett.* **1980**, *21*, 4313–4316.

57.9, 41.2, 40.3, 32.8, 25.9, 25.2, 22.1, 21.4; HRMS (EI): Exact mass calcd for $C_9H_{10}O [M]^+$, 138.1045. Found 138.1035.

(1R)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl trifluoromethanesulfonate (3): To a solution of diisopropylamine (2 mL, 14.3 mmol) in THF (50 mL) at 0 °C was added *n*-BuLi (6.67 mL, 13 mmol, 1.95 M in hexanes) and cooled to -78 °C, under N_2 . After 15 minutes, (1R)-6,6-dimethylbicyclo[3.1.1]heptan-2-one-3 (**2**) (1.8 g, 13 mmol) in THF (20 mL) was cannulated dropwise into solution of LDA and stirred for 1 hour. At this time, a solution of $PhNTf_2$ (5 g, 14 mmol) in THF (20 mL) was added over a period of 15 minutes. The resulting mixture was warmed to 0 °C and stirred for 2 hours. Reaction was diluted with H_2O (100 mL) and Et_2O (50 mL) and transferred to a separatory funnel. The organic phase was collected and the aqueous layer extracted with Et_2O (2 x 100 mL). The combined organics were dried with Na_2SO_4 . Concentration under reduced pressure and flash column chromatography on silica gel in 10% EtOAc in hexanes as the eluent afforded the title compound (2.41 g, 8.9 mmol, 69% yield) as a clear oil: 97:3 e.r. $[\alpha]^{20}_D = -53.4$ (c 2.1, $CHCl_3$); IR (film) 2958, 1420, 1206, 1143, 859 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) 5.54 (d, 1H, $J = 3.3$ Hz); 2.56 (dt, 1H, $J = 9.2, 5.7$ Hz); 2.39–2.27 (m, 3H); 2.14 (dd, 1H, $J = 5.2, 2.7$ Hz); 1.38 (d, 1H, $J = 9.2$ Hz); 1.34 (s, 3H); 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0, 118.5 (q, 1C, $J = 320$ Hz), 111.4, 46.3, 40.1, 39.7, 31.7, 28.2, 25.5, 20.8; HRMS (EI): Exact mass calcd for $C_{10}H_{13}F_3O_3S [M]^+$, 270.0538. Found 270.0538.



(1S)-6,6-Dimethyl-2-bicyclo[3.1.1]hept-2-ene (4): Methyl lithium (8.3 mL, 13.2 mmol, 1.6 M in Et_2O) was added to a slurry of CuI (1.74 g, 9.15 mmol) in Et_2O (24 mL) at 0 °C. After stirring for 15 minutes, a room temperature solution of (1R)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl trifluoromethanesulfonate (**3**) (1.02g, 3.77 mmol) in THF (6 mL) was added dropwise by cannula. After 6 hours at 0 °C, reaction was warmed to room temperature and filtered through a plug of Florisil® (CAUTION: quenches vigorously with gas evolution), flushing with pentanes. Concentration under reduced pressure afforded the title compound (450 mg, 3.30 mmol, 88% yield) as a clear oil: Spectral data matched previous information for naturally occurring pinene.

Fig. S1. ssp-Polarized high-resolution SFG spectra of synthetic (top) and commercial (-)- α -pinene at the CaF_2 /vapor interface.

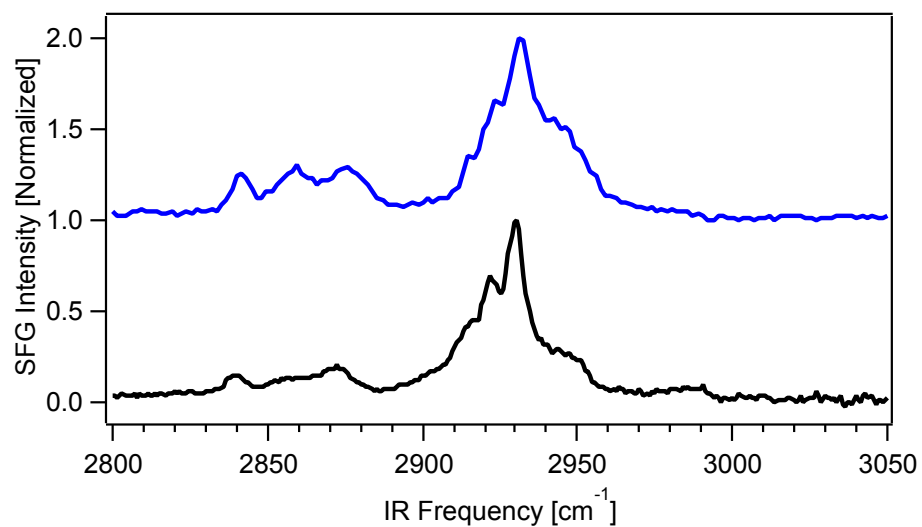
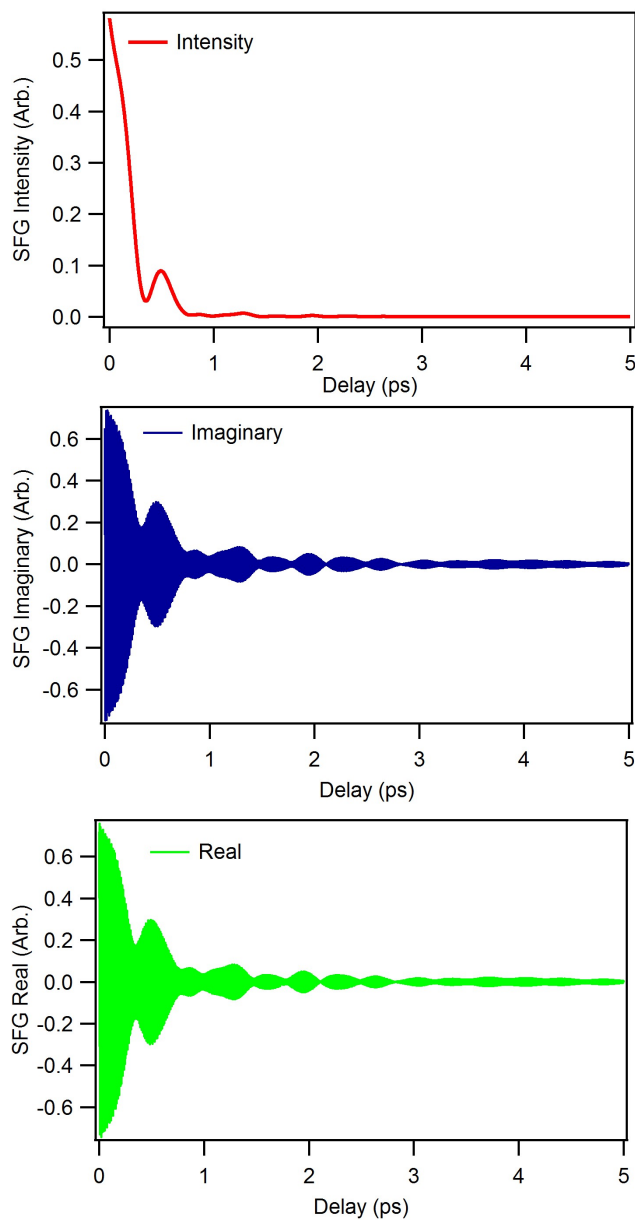


Fig. S2 Simulated time-domain SFG free-induction decay (FID) curve using the parameters of the 10 peaks in Table I. These FID curves (Intensity, Imaginary and Real) correspond to the HR-BB-SFG spectrum in Figure 3a. Due to the interference between the overlapping peaks, the FID curve is complicated and hard to be used to extract spectral parameters. However, those parameters can be obtained from fitting the HR-BB-SFG as in Figure 3a.



S2. DFTB Calculations. The method used to compute the vibrational lifetime involves the construction of a distance matrix defined by the connectivity of atoms in the molecule. $[\vec{D}]_{ij}$ refers to the distance between atoms i and j , and $[\vec{D}]_0$ denotes the distance matrix at the equilibrium geometry. The time-dependent fluctuation of the distance matrix is shown in Eqn (S2).

$$[\vec{D}]_{ij} = |\vec{r}_i - \vec{r}_j| \quad (S1)$$

$$[\vec{f}](t) = [\vec{D}](t) - [\vec{D}]_0 \quad (S2)$$

$$[\vec{f}]_s = [\vec{D}]_s - [\vec{D}]_0 \quad (S3)$$

$$P(t) = \sum_i^{N_{atom}} \sum_j^{N_{atom}} [\vec{f}]_{ij}(t) [\vec{f}]_{ij,s} \quad (S4)$$

Additionally, a *static* displacement matrix $[\vec{f}]_s$ is defined where the molecular geometry is displaced by a specific step size along a selected normal mode, and $[\vec{D}]_s$ is the distance matrix at the displaced geometry. Projection of the time-dependent fluctuation matrix $[\vec{f}](t)$ onto $[\vec{f}]_s$ is obtained from the sum of the dot products of corresponding column vectors in $[\vec{f}](t)$ and $[\vec{f}]_s$ as shown in Eqn (S4).

Using the procedure described above, a selected normal mode is “excited” at the start of the simulation by displacing the molecule from its minimized geometry along that mode using a step size of 0.0625 Å. $P(t)$ is monitored as a function of time, and its Fourier transform yields a spectrum with a well-defined peak at the vibrational frequency of that normal mode. The peak is fitted to a Lorentzian and the lifetime is estimated from the reciprocal of the full width at half-maximum. We have verified that the lifetime calculations are *generally* not sensitive to the choice of step size (See Table S1). We have also tested the effect of varying the coupling strength (0.05, 0.1 and 0.2 ps⁻¹) to the Berendsen thermostat for two modes and verified that the effect is generally small. Specifically, for the resulting lifetimes for the νCH₃ symmetric stretch are 0.68, 0.88 and 0.61 ps respectively. Similarly, the lifetimes for the βCH₂ symmetric stretch are 1.7, 1.9 and 1.6 ps respectively. As such, all calculations were based on the coupling strength of 0.1 ps⁻¹. All geometry optimization and frequency calculations (B3LYP and DFTB) were carried out in Gaussian 09¹ using the “mio-1-1” parameter set.² The DFTB molecular dynamics simulations were carried out using the DFTB+ program.³

Table S1. Dependence of computed vibrational lifetimes on stepsize.

Mode	$\langle t \rangle$ /ps ^a	Stretch size(Å) ^b	Energy (kcal mol ⁻¹) ^c
νCH ₃ sym str	0.5	0.5	178.3
	0.5	0.25	31.5
	0.8	0.125	6.9
	0.9	0.0625	1.9

$\eta,\chi\text{CH}_3$ sym str	1.1	0.5	145.4
	0.5	0.25	28.6
	0.7	0.125	6.8
	1.1	0.0625	2.0
βCH_2 sym str	1.6	0.5	150.9
	1.5	0.25	28.8
	1.5	0.125	6.4
	1.9	0.0625	1.7
$\eta,\chi\text{CH}_3$ asym str	1.1	0.5	151.6
	1.6	0.25	30.0
	1.8	0.125	7.4
	3.3	0.0625	2.2

^a Averaged over five 6 ps trajectories. ^b Displacement along selected normal mode (angstrom). ^c Energy of the stretched configuration relative to minimum at the DFTB level of theory

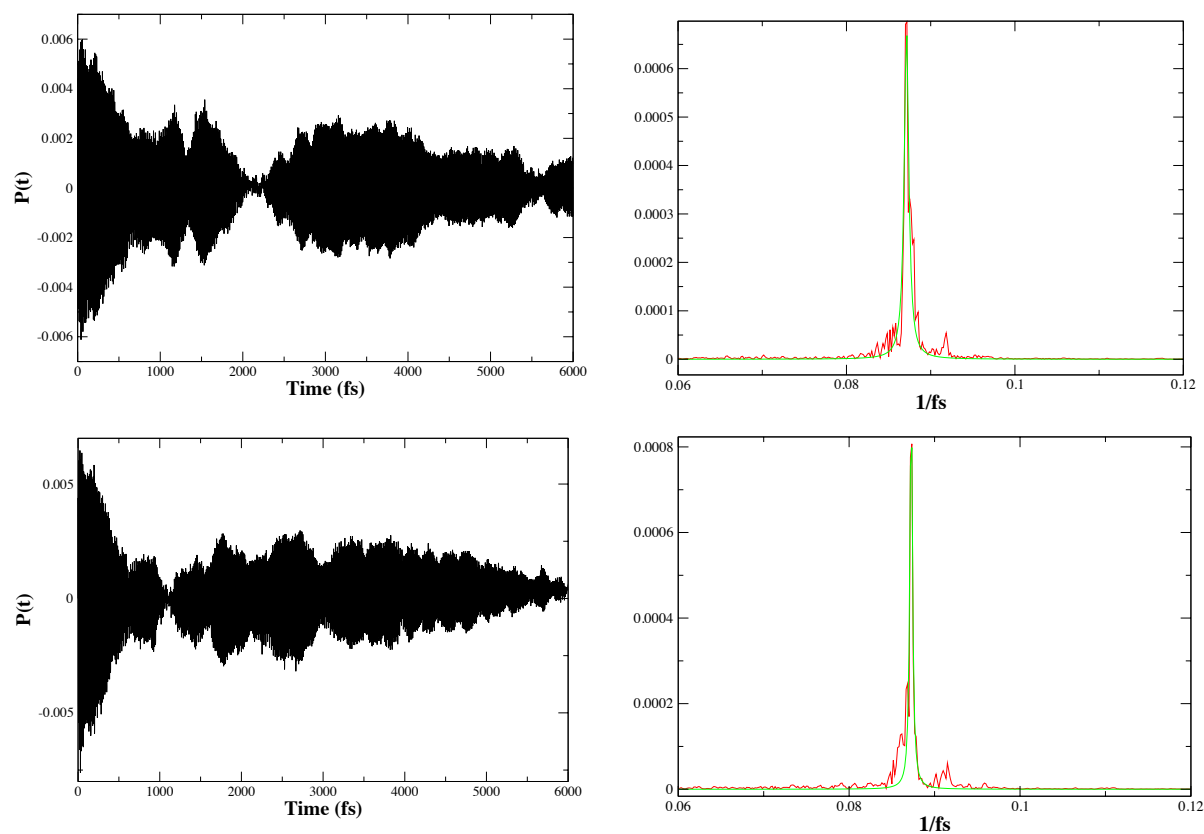


Fig. S3. LEFT: Decay of displacement along normal mode $\eta,\chi\text{CH}_3$ symmetric stretch (top) and βCH_2 symmetric stretch (bottom). RIGHT: Corresponding Lorentzian fit to the Fourier transform of $P(t)$.

S3. References

- (S1) Gaussian 09, R. A., Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
- (S2) Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, M.; Haugk, M.; Frauenheim, T.; Suhai, S.; Seifert, G. *Phys. Rev. B* **1998**, 58, 7260.
- (S3) Aradi, B.; Hourahine, B.; Frauenheim, T. *J. Phys. Chem. A* **2007**, 111, 5678.