Supporting Information for

On Surface Order and Disorder of α-Pinene-Derived Secondary Organic Material

Mona Shrestha,[1] Yue Zhang,[2] Mary Alice Upshur,[1] Pengfei Liu,[2] Sandra L. Blair,[3] Hong-fei Wang,[4] Sergey A. Nizkorodov,[3] Regan J. Thomson,[1] Scot T. Martin,[2,] and Franz M. Geiger[1,*]*

[1]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA; [2]School of Engineering and Applied Sciences & Department of Earth and Planetary Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, USA; [3]Department of Chemistry, University of California, 1102 Natural Sciences 2, Irvine, CA, 92697, USA; [4]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, 3335 Innovative Boulevard, Richland, WA 99354, USA

Table SI. Concentration of volatile precursors, collection time and type (Teflon vs. optical window) utilized for the preparation of SOM particle samples relevant for this study along with the total majority and minority responses for each sample.

Sample	[(+)-α-pinene] (ppb)	[ozone] (ppm)	Collection time	Majority response	Minority Response	Type
1	125	50	523 min	10	2	Teflon
2			83 hrs	5	2	
3	700	14	31 min	3	3	Window
4			122 min	11	1	

Table SII. Screenshot of the table showing the refractive indices of air at 0% and 100% RH for the Fresnel coefficient calculations[1]

Temperature (Celsius)	Relative Humidity (%)	Pressure (kPa)	Wavelength (nm)	Index of Refraction (Ciddor)	Index of Refraction (Modified Edlén)	Difference $\times 10^5$ (Ciddor-Edlén)
20	0	101.325	633	1.000271800	1.000271799	0.1
20	0	60	633	1.000160924	1.000160920	0.4
20	0	120	633	1.000321916	1.000321918	-0.2
50	0	100	633	1.000243285	1.000243270	1.5
5	0	100	633	1.000282756	1.000282750	0.6
-40	0	100	633	1.000337580	1.000337471	10.9
50	100	120	633	1.000287924	1.000287864	6.0
40	75	120	633	1.000299418	1.000299406	1.2
20	100	100	633	1.000267394	1.000267394	0.0
40	100	110	1700	1.000270247	1.000270237	1.0
20	0	101.325	1700	1.000268479	1.000268483	-0.4
40	100	110	300	1.000289000	1.000288922	7.8
20	0	101.325	300	1.000286581	1.000286579	0.2
-40	0	120	300	1.000427233	1.000427072	16.1

Table 1. Index of refraction as calculated using the Modified Edlén equation and Ciddor equation, assuming 450 µmol/mol CO_2 concentration. The vapor pressure and mole fraction for 100 % humidity is calculated using the IAPWS equation. Values for the index given in the table have one or two significant figures more than can be

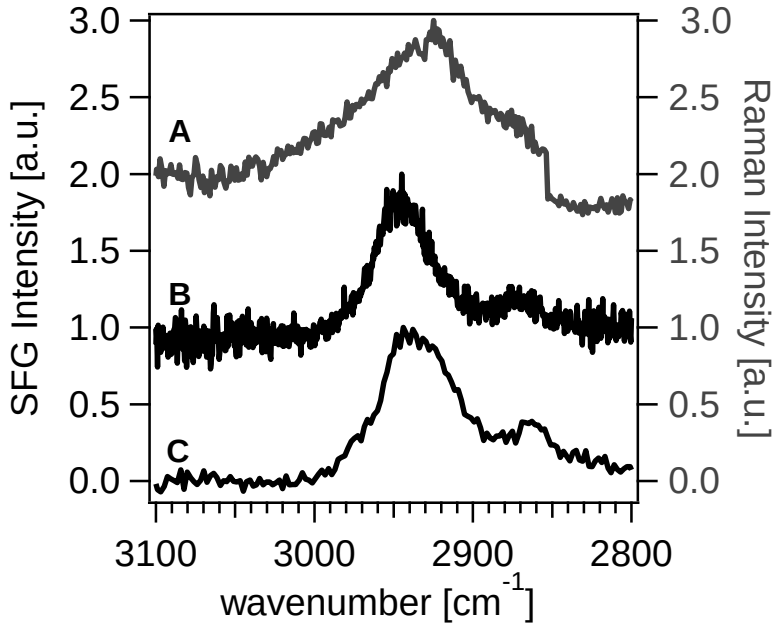

Figure SI. SFG spectra collected at (B) PNNL and (C) NU are qualitatively similar to what is observed in the Raman spectrum (A) in the C-H stretching region. All the spectra have been normalized to their maximum intensity and are offset for clarity.

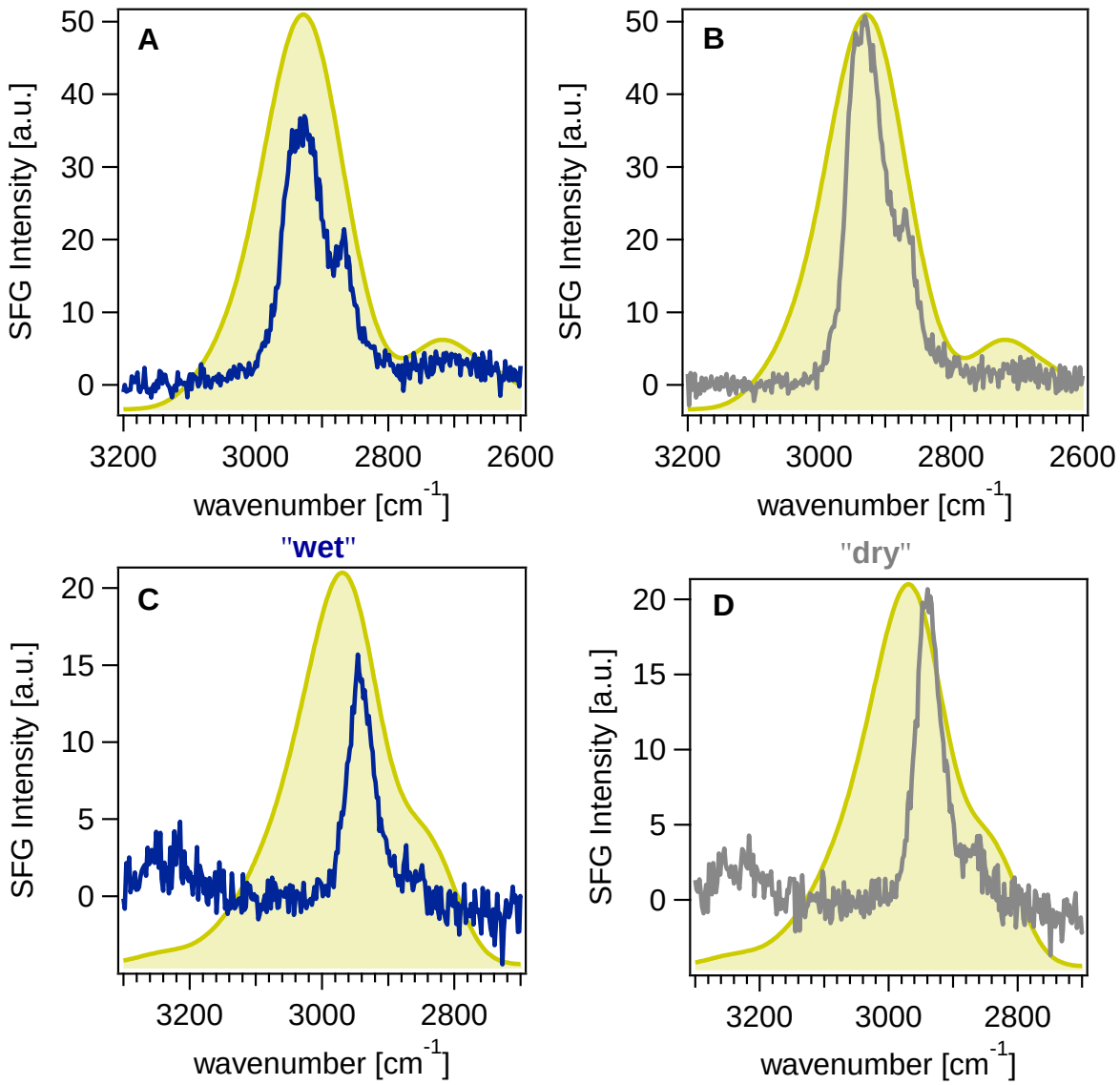

Figure SII. ssp-Polarized vibrational spectra recorded after performing RH experiments with D_2O (A, B) and H_2O (C, D) with the corresponding gold spectrum (in yellow) for two different particle samples. Some H_2O and D_2O is present as shown further supporting the claim of negligible spectral interference between O-H/O-D and C-H stretches as the cause for the observed RH-dependent SFG signal intensity changes discussed in the main text. SFG spectra (A, B) and (C, D) are plotted from 3200 cm^{-1} - 2600 cm^{-1} and 3300 cm^{-1} - 2700 cm^{-1}, respectively to highlight the presence of D_2O and H_2O in the spectra above.

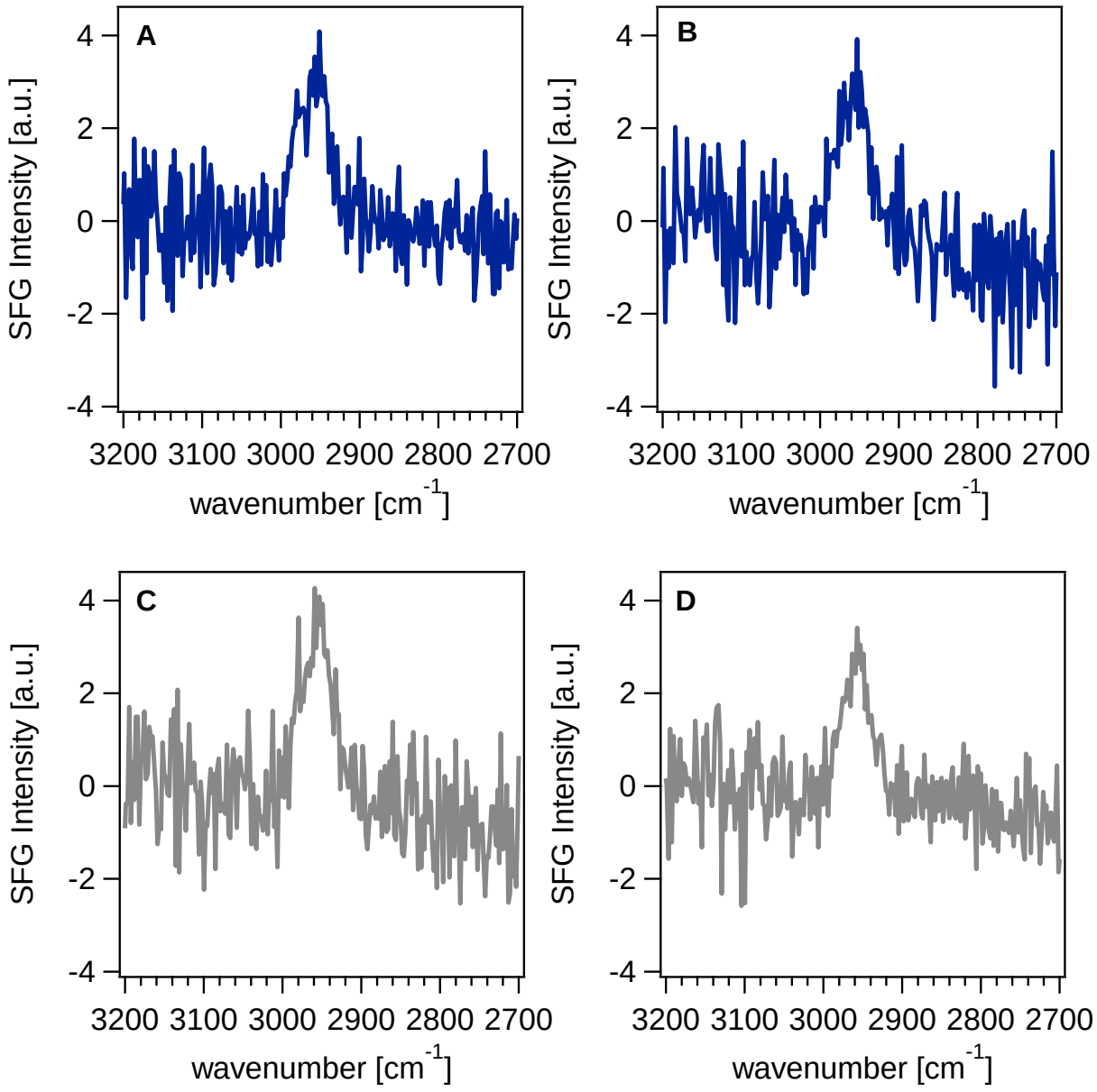

Figure SIII. ppp-Polarized vibrational SFG spectra recorded at ~95% (A,B) and <2% (C,D) RH from α-pinene-derived SOM for two RH jumps (A,C and B, D).

References:

(1) Stone, J. A.; Zimmerman, J. H. 2001; Vol. 2014. http://emtoolbox.nist.gov/Wavelength/Documentation.asp (accessed on May 6, 2014)