

Supporting Information

Structure of butanol and hexanol at aqueous, ammonium bisulfate, and sulfuric acid solution surfaces investigated by vibrational sum frequency generation spectroscopy

Lisa L. Van Loon, Rena N. Minor, and Heather C. Allen*

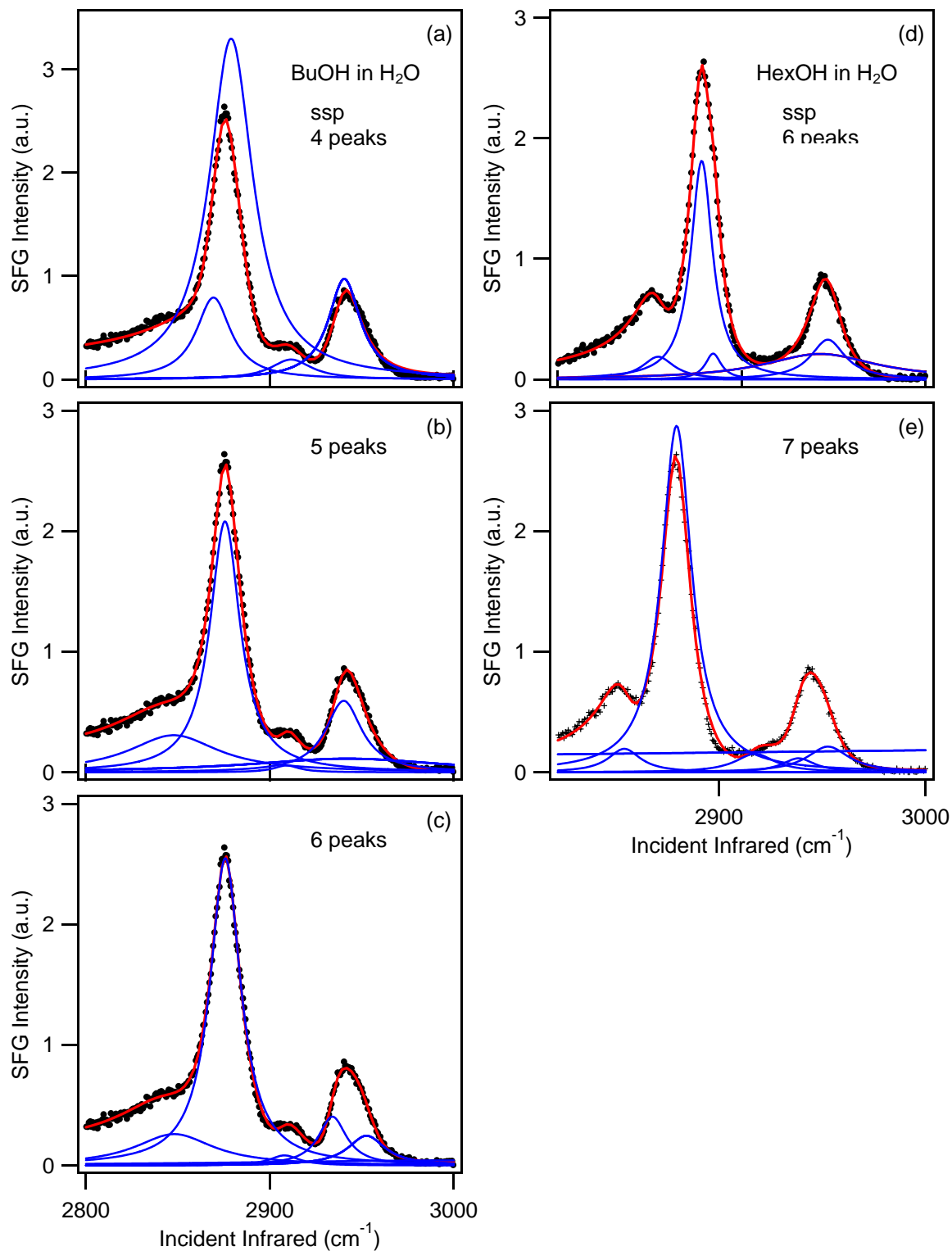
Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210

(Chemical abbreviations used in this paper are BuOH (butanol), HexOH (hexanol), and SA (sulfuric acid). In addition, vibrational sum frequency generation (VSFG), broad bandwidth sum frequency generation (BBSFG), symmetric stretch (ss), and asymmetric stretch (as) are used.

Fitting of the VSFG spectra

The ssp VSFG spectra of the BuOH solutions were fit with four, five (to include a contribution from water), and six (to include $\nu_{\text{CH}_3\text{-as}}$) component peaks to determine the best overall fit. The 0.50 M BuOH in water ssp SFG spectrum is shown in Figure SI-1 three times to show the differences in the fits. The four-component peak fit (a) considers only the expected BuOH peaks. The five-component peak fit (b) gave the best overall fit by including a contribution from water. Adding a sixth component peak to include a contribution from the methyl asymmetric stretch (c) did not improve the overall fit. The 0.050 M HexOH in water ssp SFG spectrum is also shown in Figure SI-1 fit with (d) six and (e) seven component peaks. The six-component peak fit comprises only the expected HexOH peaks. Allowing for a water contribution, using seven component peaks gave the best overall fit.

Figure SI-1. Peak fits of (a-c) the ssp VSGF spectrum of 0.50 M BuOH in H₂O with (a) four, (b) five, and (c) six component peaks, and (d-e) the ssp VSGF spectrum of 0.050 M HexOH in H₂O with (d) six, and (e) seven component peaks. The original spectrum is shown as black data points, the overall fit is shown as the red line going through the data points, and the component peaks are shown in blue.



To determine the peak positions of each vibrational mode, the ssp, ppp, and sps VSG spectra were fit with the appropriate component peaks. If a peak contribution was very small, i.e., the CH₃-ss in the ppp spectra, the position was held (see Tables SI 1-4). The fitted 0.50 M BuOH in water ssp, ppp, and sps VSG spectra are shown in Figure SI-2. The ssp spectrum (a) is fit with five peaks, the ppp spectrum (b) is fit with three peaks, and the sps spectrum (c) is fit with two peaks. The fitted peak positions and assignments are shown in Tables SI 1-4.

Figure SI-2. Fitting of the (a) ssp, (b) ppp, and (c) sps SFG spectrum of 0.50 M BuOH in H₂O The original spectrum is shown as black data points, the overall fit is shown in red, and the component peaks are shown in blue.

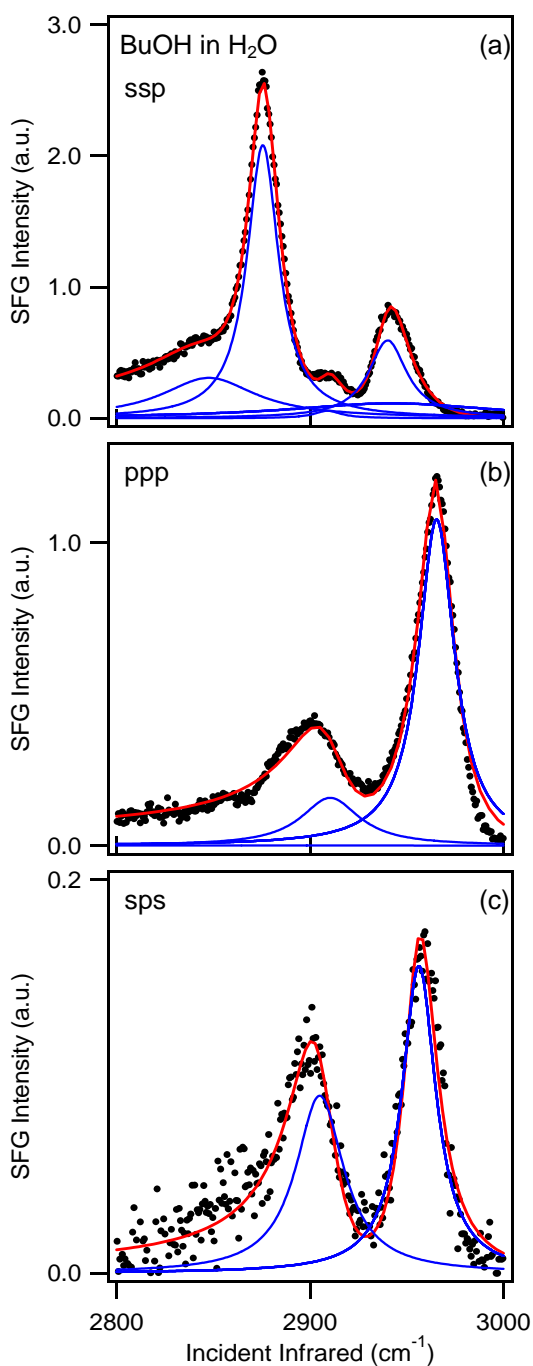


Table SI-1. Vibrational mode assignments for neat BuOH and neat HexOH with fitted peak positions.

Peak positions held during the spectral fitting are indicated by (h).

	CH ₂ -ss	CH ₃ -ss	CH ₂ -as	CH ₂ -FR	CH ₃ -FR	CH ₃ -as
1-Butanol						
ssp	2846	2877		2908	2941	
ppp		2880(h)	2909			2966
sps			2889			2961
1-Hexanol						
ssp	2856	2878		2903/2922/2947	2939	
ppp		2880(h)	2920			2970
sps			2915			2961

Table SI-2. Vibrational mode assignments for BuOH and HexOH solutions in water with fitted peak positions. Peak positions held during the spectral fitting are indicated by (h).

	vCH ₂ -ss	vCH ₃ -ss	vCH ₂ -as	CH ₂ -FR	CH ₃ -FR	vCH ₃ -as
1-Butanol						
0.50 M						
ssp	2833	2879		2914	2941	
ppp		2885	2913			2973
sps			2908			2965
0.179 M						
ssp	2836	2876		2907	2938	
ppp		2880(h)	2910			2968
sps			2901			2955
0.052 M						
ssp	2848	2876		2919	2940	
ppp		2887(h)	2910			2965
sps			2905			2956
1-Hexanol						
0.050 M						
ssp	2854	2879	2917/2931/2953	2938		
ppp		2880(h)	2912			2969
0.0099 M						
ssp	2850	2879	2912/2925/2946	2938		
ppp		2880(h)	2912			2966
0.0051 M						
ssp	2852	2880	2909/2924/2947	2941		
ppp		2880(h)	2914			2966

Table SI-3. Vibrational mode assignments for BuOH and HexOH solutions in 0.78 M NH₄HSO₄ with fitted peak positions. Peak positions held during the spectral fitting are indicated by (h).

	CH ₂ -ss	CH ₃ -ss	CH ₂ -as	CH ₂ -FR	CH ₃ -FR	CH ₃ -as
1-Butanol						
0.50 M						
ssp	2835	2880		2912	2943	
ppp		2877	2902		2940	2962
sps			2905			2958
0.179 M						
ssp	2841	2878		2905 (h)	2941	
ppp		2880(h)	2916			2974
sps			2906			2956
0.052 M						
ssp	2835	2880		2912	2943	
ppp		2880(h)	2908			2969
sps			2905			2958
1-Hexanol						
0.050 M ssp	2852	2876		2881/2912/2974	2938	
0.0099 M ssp	2852	2876		2883/2912/2951	2937	
0.0051 M ssp	2853	2876		2883/2914/2951	2937	

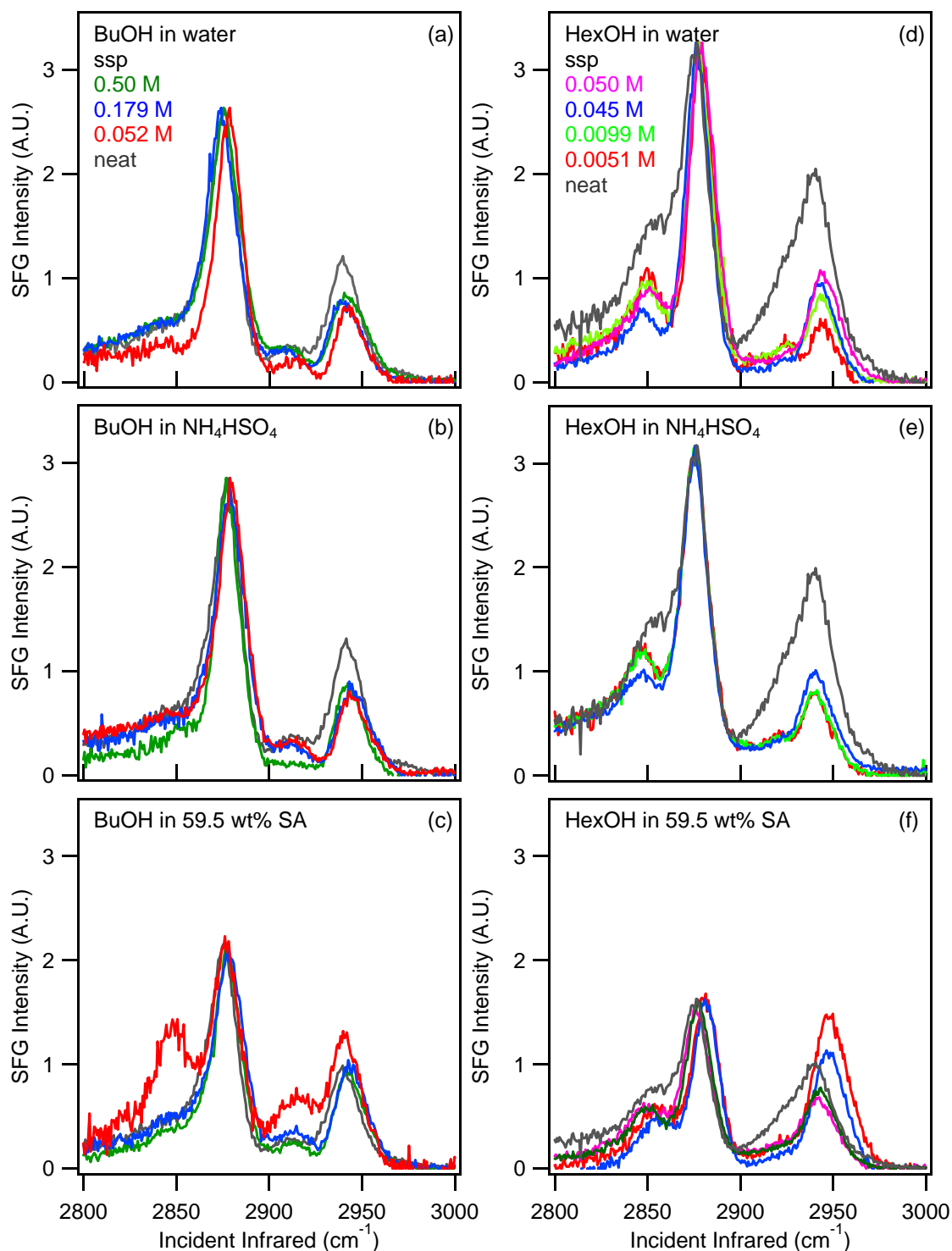
Table SI-4. Vibrational mode assignments for BuOH and HexOH solutions in 59.5 wt% SA with fitted peak positions. Peak positions held during the spectral fitting are indicated by (h).

	CH ₂ -ss	CH ₃ -ss	CH ₂ -as	CH ₂ -FR	CH ₃ -FR	CH ₃ -as
1-Butanol						
0.50 M						
ssp	2848	2879		2912	2941	
ppp		2880(h)	2918			2969
sps			2911			2962
0.179 M						
ssp	2848(h)	2884		2915	2946	
ppp		2880(h)	2923			2970
sps			2920			2965
0.052 M						
ssp	2853	2879		2915	2939	
ppp	2866	2885(h)	2898		2925	2969
sps			2908			2970
1-Hexanol						
0.050 M ssp	2853	2878		2885/2903/2915	2945	
0.0099 M ssp	2858	2880		2885/2919/2952	2940	
0.0051 M ssp	2858	2878		2884/2901/2913	2946	

Normalization of spectral to methyl symmetric stretch

The butanol and hexanol solution ssp spectra were normalized to the most intense methyl symmetric stretch to compare spectral differences. The normalized spectra are shown in Figure SI-3.

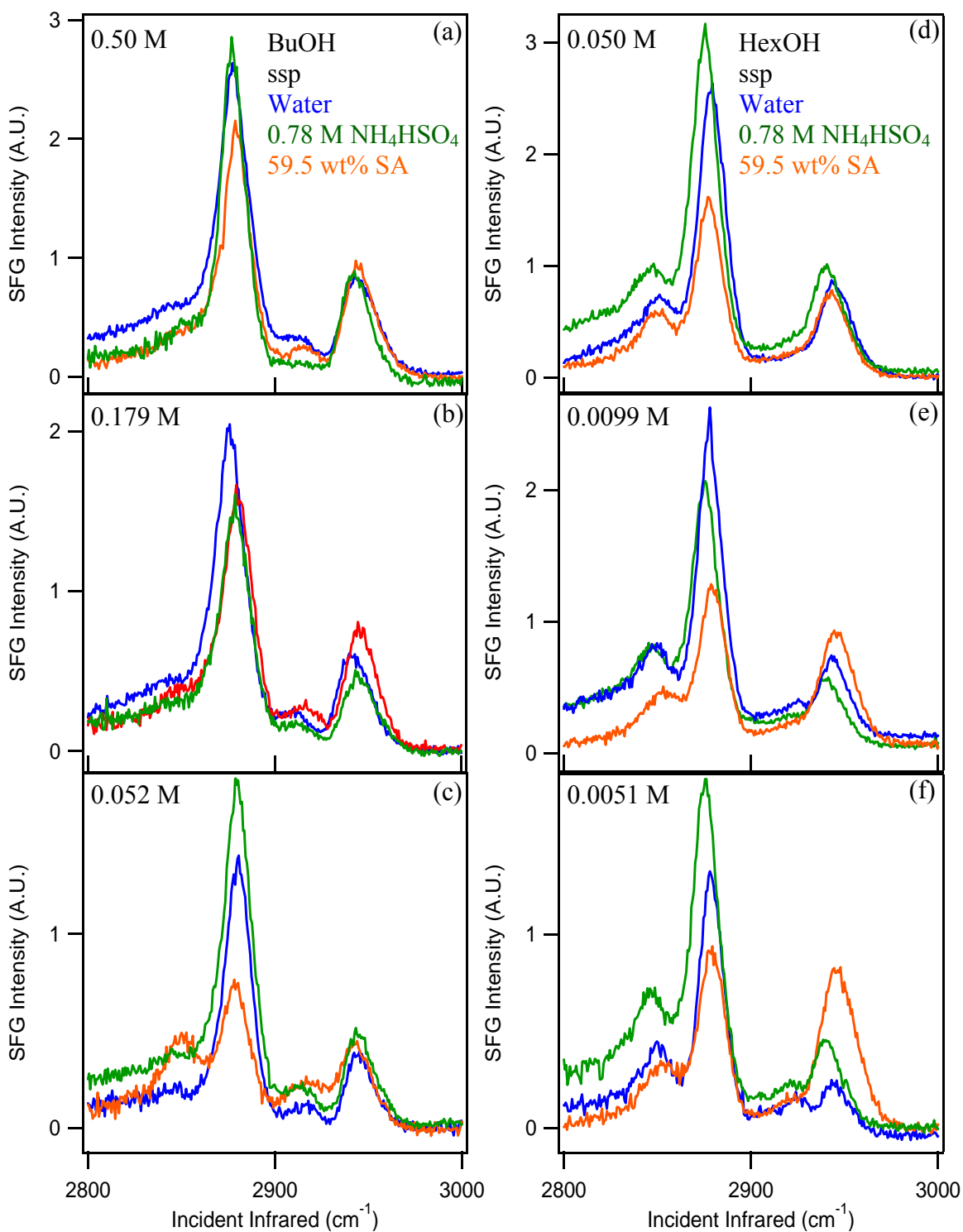
Figure SI-3. VSFG ssp spectra of BuOH (a-c) and HexOH (d-f) solutions in water, 0.78 M NH_4HSO_4 , and 59.5 wt% SA normalized to the CH_3 -ss.



Comparison of solvents

The differences in the ssp polarization spectra for each concentration of BuOH and HexOH were examined as a function of solvent. The spectra are shown in Figure SI-4.

Figure SI-4. VSFG ssp polarization spectra of (a-c) BuOH solution and (d-f) HexOH solution. The water solutions are shown in blue, the 0.78 M NH_4HSO_4 solutions are shown in green, and the 59.5 wt% SA solutions are shown in orange.



Parameters for determination of θ

The orientation calculations require the input of several system-dependant variables, including the indices of refraction, the input beam wavelengths and incident angles, and the hyperpolarizability ratio (R) for the functional group being studied. The index of refraction of neat butanol used was $n = 1.3973$.¹ The index of refraction for each BuOH-water solution was extrapolated from data found in the literature.² The BuOH-NH₄HSO₄ solutions were assumed to have the same indices of refraction as the comparable water solutions. The value of n for the sulfuric acid solutions used was the index of refraction for 60 wt % SA at 2880 cm⁻¹.³ All of the values for n used are found in Table SI-5. The visible beam wavelength was 799.8 nm. The IR peak chosen was the CH₃-ss at 2880 cm⁻¹. The hyperpolarizability ratio for the methyl group used was $R = 3.4$.⁴ The experimental incident angles are also found in Table SI-5. From this information the $\chi_{\text{eff}}(\text{ssp})$ and $\chi_{\text{eff}}(\text{ppp})$ for the symmetric stretch are

calculated as a function of orientation angle, θ . A typical plot of the ratio of $\frac{\chi_{\text{effective}} - \text{ssp} - \text{SS}(\theta)}{\chi_{\text{effective}} - \text{ppp} - \text{SS}(\theta)}$ vs θ

is shown in Figure SI-6. The ratio of the square root of the intensities of the CH₃-ss in the ssp and ppp

spectra, $\sqrt{\frac{I_{\text{ssp,ss}}}{I_{\text{ppp,ss}}}}$, is calculated. From the plot, the angle corresponding to that ratio is the terminal

methyl orientation angle. Once the orientation angle is known, the chain tilt angle can also be calculated

as $\alpha = |35.5 - \theta_{\text{CH}_3}|$. The calculated BuOH methyl orientation angles and chain tilt angles are found in

Table SI-6.

Table SI-5. Variables used in the calculation of the methyl orientation angle, θ .

$\theta_{\text{vis}} = 58^\circ$	$n_{\text{neat}}^1 = 1.3973$	$n_{0.052 \text{ in H}_2\text{O}} = 1.3325$
$\theta_{\text{IR}} = 66^\circ$	$n_{\text{SA}}^3 = 1.37624$	$n_{0.179 \text{ in H}_2\text{O}} = 1.3334$
		$n_{0.50 \text{ in H}_2\text{O}} = 1.3358$

Figure SI-6. Typical plot of $\frac{\chi_{effective_ssp_SS}(\theta)}{\chi_{effective_ppp_SS}(\theta)}$ vs θ . The terminal methyl orientation angle, θ , is

read off the plot for the appropriate value(s) of the ratio.

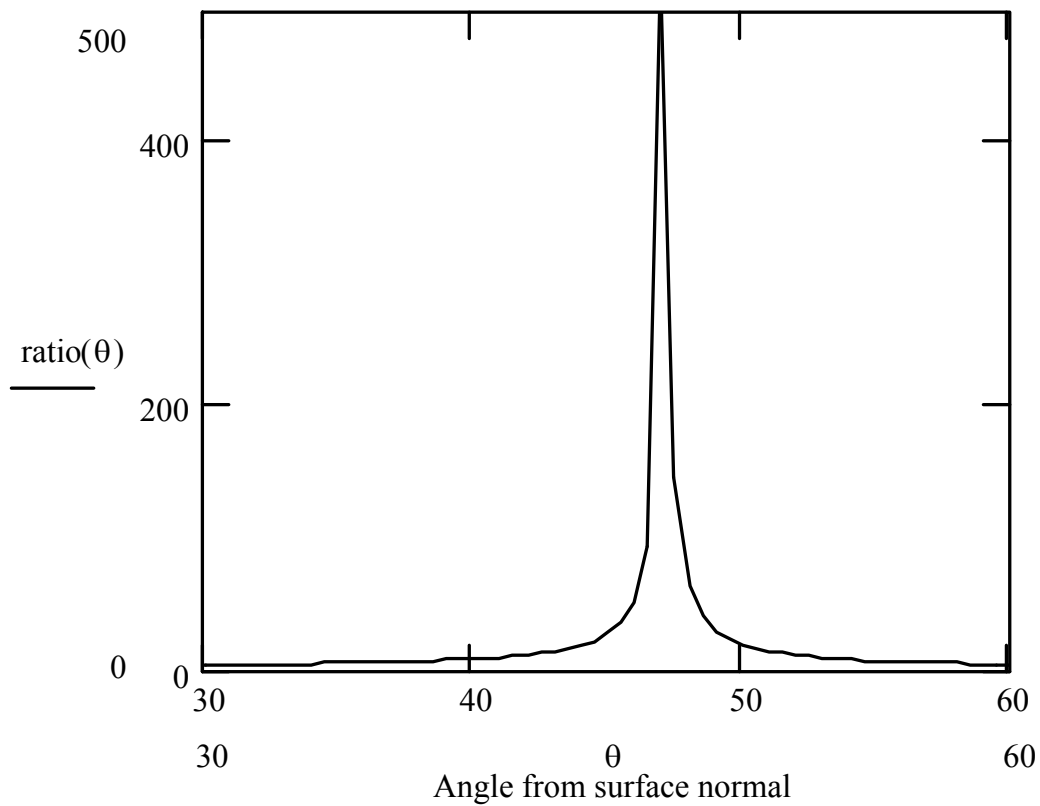


Table SI 6. Calculated orientation angles for the 1-butanol methyl group, θ_{CH_3} , and the butanol chain tilt angles, α .

	θ_{CH_3}	α		θ_{CH_3}	α		θ_{CH_3}	α
neat	57	21.5						
Water			59.5 wt % SA			0.78 M NH_4HSO_4		
0.50 M	44.5	9	0.50 M	46.5	11	0.50 M	47	9.5
0.179 M	39.5	4	0.179 M	48.5	13	0.179 M	42.5	7
0.052 M	46.5	11	0.052 M	67	31.5	0.052 M	41	5.5

References

- (1) McKenna, F. E.; Tartar, H. V.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1953**, *75*, 604-607.
- (2) Fuoss, R. M. *J. Am. Chem. Soc.* **1943**, *65*, 78-81.
- (3) Palmer, K. F.; Williams, D. *Appl. Optics* **1975**, *14*, 208-219.
- (4) Wang, H.-f.; Gan, W.; Lu, R.; Rao, Y.; Wu, B.-H. *Int. Rev. Phys. Chem.* **2005**, *24*, 191-256.