Sum Frequency Vibrational Spectroscopy of the Liquid-Air Interface of Aqueous Solutions of Ethanol in the OH Region

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The surface vibrational spectroscopy of ethanol (C_2H_5OH, ethyl alcohol): water binary mixture, or the aqueous solution of ethanol, is investigated via sum frequency generation (SFG) in the OH region (3000 to 3900 cm^{-1}). The bulk molar ratio of the ethanol is varied from x = 0.0024 to 0.20. Our concentration dependence results support the statement that the surface density of water molecules with a free dangling OH bond is about 25% in the air/water interface. It also indicates that the ethyl group of the surface ethanol molecules sticks out above the nominal surface, while the hydroxyl group alone is immersed in the mixture solution. And the surface layer is a mixed monolayer. We have demonstrated here that a $LiNbO_3$ crystal containing -OH can be sufficient for the SFG spectroscopy measurement in the -OH region regardless of its absorption dip.

INTRODUCTION

Sum frequency generation (SFG) is a surface sensitive tool pioneered by Shen.[1] The surface specificity arises from the sensitivity toward the breaking down of the inversion symmetry at the surface or interface, while centrosymmetry tends to prevail in the bulk medium. A molecular vibration has to be both infrared allowed and Raman active in order to have resonance enhanced contribution to the second-order nonlinear susceptibility $\chi^{(2)}$, the square of which is proportional to the intensity of the SFG signal. Yet this cannot possibly be true for a centrosymmetric molecule, medium, material or bulk: either the infrared transition dipole moment or the derivative of the Raman polarizability will have to vanish. Therefore there is no bulk contribution for the SFG in the electric-dipole approximation. While the bulk effect that comes from the electric quadrupole moment or the magnetic dipole moment can usually be ignored or suppressed relative to the surface contribution, the forbidden SFG only occurs in centrosymmetric medium with electrons confined to the neighborhood of a nearby nucleus under large field gradient across the interface.[2]

The liquid interface study via SFG was also pioneered by Shen.[3,4,5] Shen's group,[6] followed by other groups[7,8] has obtained the air (liquid)/water SFG spectra. They assigned the 3200, 3400 cm^{-1} broad features to be OH stretches associated with the OH hydrogen-bonded to neighbors, and the 3680 cm^{-1} peak to be OH stretch associated with free dangling OH bonds. Methanol and ethanol have also been investigated.[9] Upon mixing methanol with water, the peak strength of the 3680 cm^{-1} is observed to be decreased, and completely depleted when the bulk concentration of 11% in volume is reached for the methanol in mixture.[6] That corresponds to a bulk molar ratio around 5.2% (x = 0.052) and a surface concentration of 25% (x = 0.25)[3] according to Shen's interpretation[3] of Kipling's calculated adsorption isotherm based on surface tension measurements.[10] While our value of surface density is 29% for bulk x = 0.052 extracted from the same isotherm.

The surface vibrational spectra of methanol:water binary mixture in the -CH region via SFG has been published by Huang and Wu[11] and Laubereau et al.[12] As for the ethanol (C_2H_5OH):water mixture, Klein et al.[13,14] have examined the 0.1 M (about 0.18% or x = 0.0018) solution in liquid/vapor interface via molecular dynamic simulation. The segregation of the ethanol at the surface is observed, in agreement with the neutron reflectivity measurements.[15] Recent surface tension measurements[16,17] and calculated adsorption isotherms[18] are also available for the aqueous solution of ethanol, yet for the purpose of comparison with the SFG work of Shen et al.

and Laubereau's group, we stay with Kipling's isotherm in the discussion section.

EXPERIMENTAL

Our SFG apparatus is a slight modification of the one reported by Huang and Shen.[19] The pumping source, Continuum PY 61C-20: Nd YAG mode locked laser generates 35 picoseconds, 1064 nm, 35 mJ pulse at 20 Hz repetition rate. The laser output is split into three branches: 1) 20% of the power is split first to pump a $LiNbO_3$ optical parametric generator (OPG) system, 2) 40% of the power, combined with the OPG output, is used for the $LiNbO_3$ optical parametric amplifier (OPA), yielding tunable infrared pulses with tuning range of 2400-3900 cm^{-1} which can cover the C-H and O-H stretching regions. 3) The residual beam with 40% energy propagates further through a LBO frequency doubler, producing the 532 nm visible light.

The visible light and the infrared beam (idler only) are overlapped over the sample surface, where the sum frequency generation (SFG) occurs and propagates along with the visible light that is reflecting away from the sample surface towards the detection system. The overlapping alignment is optimized at 3400 cm^{-1}. Pulse energies were 160 μJ for the IR and 1.2 mJ for the visible. Angles of incidence with respect to the surface normal were 55° and 40° for the infrared and visible. The IR beam was focused into 0.5 mm spot diameter, and the visible was focused deliberately below the sample surface so that the spot diameter on the plane is equal to 2 mm. This is to ensure that the IR beam always moves inside the green beam to avoid walk-off effect during the angle-tuning of $LiNbO_3$ crystals.

The detection system for the SFG consists mainly of a Hamamatsu R955 photomultiplier tube. Spatial filtering and two pieces of OMEGA optical filter 465DF55 are used to suppress the 532 nm scattered light. A 30 cm lens is inserted to reshape the divergent SFG beam, followed by a second 5 cm lens to collimate the beam again in front of the PMT.

Our $LiNbO_3$ crystal is not hydroxyl (OH) free, and an absorption dip due to this lies on 3491 cm^{-1}. The crystal dip, a mica film, and a polystyrene film are used as direct calibration standards for the idler frequencies.

A ZnSe filter is used to separate the 1064 nm pumping beam and the IR beams (including both the signal and the idler). The second harmonic generation of the signal beam occurs on the ZnSe filter as well, and is sent into a photodiode behind a Jobin Yvon H20 monochromator. It serves as the indirect calibration standard for the idler beam.

All of the above calibrations, direct or indirect, are performed simultaneously with the measurements of the SFG signals to minimize time drifting.

The crystal dip eventually does not jeopardize our SFG spectrum of solution samples, since we are able to correct this by normalizing the liquid spectrum with the SFG spectrum of a y-cut crystal line quartz plate that is placed at the sample position before or after the measurements for the liquid samples are taken.

The water we use is deionized water with 18.2 MΩ/cm resistivity from a Millipore filtration system, while spectral grade ethanol is purchased from Merck. Like Laubereau et al.[12] our air/liquid results are carried out at room temperature under normal conditions. They did rule out the possibility of surface contamination for the air/methanol:water case, since no changes were seen for SFG spectra with nitrogen purging. We assume this is true for the case of air/ethanol:water as well. All of the mixtures samples are freshly made before the measurements. The bulk concentration of the ethanol is varied in the range from x = 0.0024 to x = 20. Neat water (x = 0) and ethanol (x = 1) spectra are also repeated here. A teflon cell is used as the liquid sample container.

RESULTS AND DISCUSSION

The polarization combination of s-s-p for sum frequency (s), green (s) and idler output (p) is used for all of the SFG spectra presented here. Fig. 1 shows our concentration dependence of the ethanol:water SFG spectra in the air/liquid interface.

We can see that along with the raising of the ethanol bulk concentration, the sharp feature in our SFG spectra due to the free OH stretch disappears into a broad flat feature gradually, just like what happens in methanol:water. It is completely flat when it reaches x = 1.6% and higher. The sharp feature peaks at 3721 cm^{-1} instead of 3680 cm^{-1} for our neat water, and peak position varies for mixtures of various concentrations (see Table 1).

In Kipling's paper[10] two adsorption isotherms exist for the ethanol:water solution, and they predict different bulk concentration for the ethanol surface concentration to reach 25%, which is the ratio that the sharp 3680 cm^{-1} band for free OH stretch to disappear in a methanol:water solution. Shen's speculation is that one surface methanol molecule can eliminate one dangling OH; therefore, the surface density of the water molecules that carry a dangling bond must be 25% as well. If this "one alcohol to one dangling bond" relation applies to ethanol:water equally well, we then expect to see the

OH dangling bond to diminish at the same ethanol surface concentration.

The two different isotherms of ethanol:water mixtures,[10] labeled here **I** and **II**, correspond to two different conditions for a n-alkyl alcohol to stand above the liquid surface:

Isotherm I is based on a condition where an n-alkyl

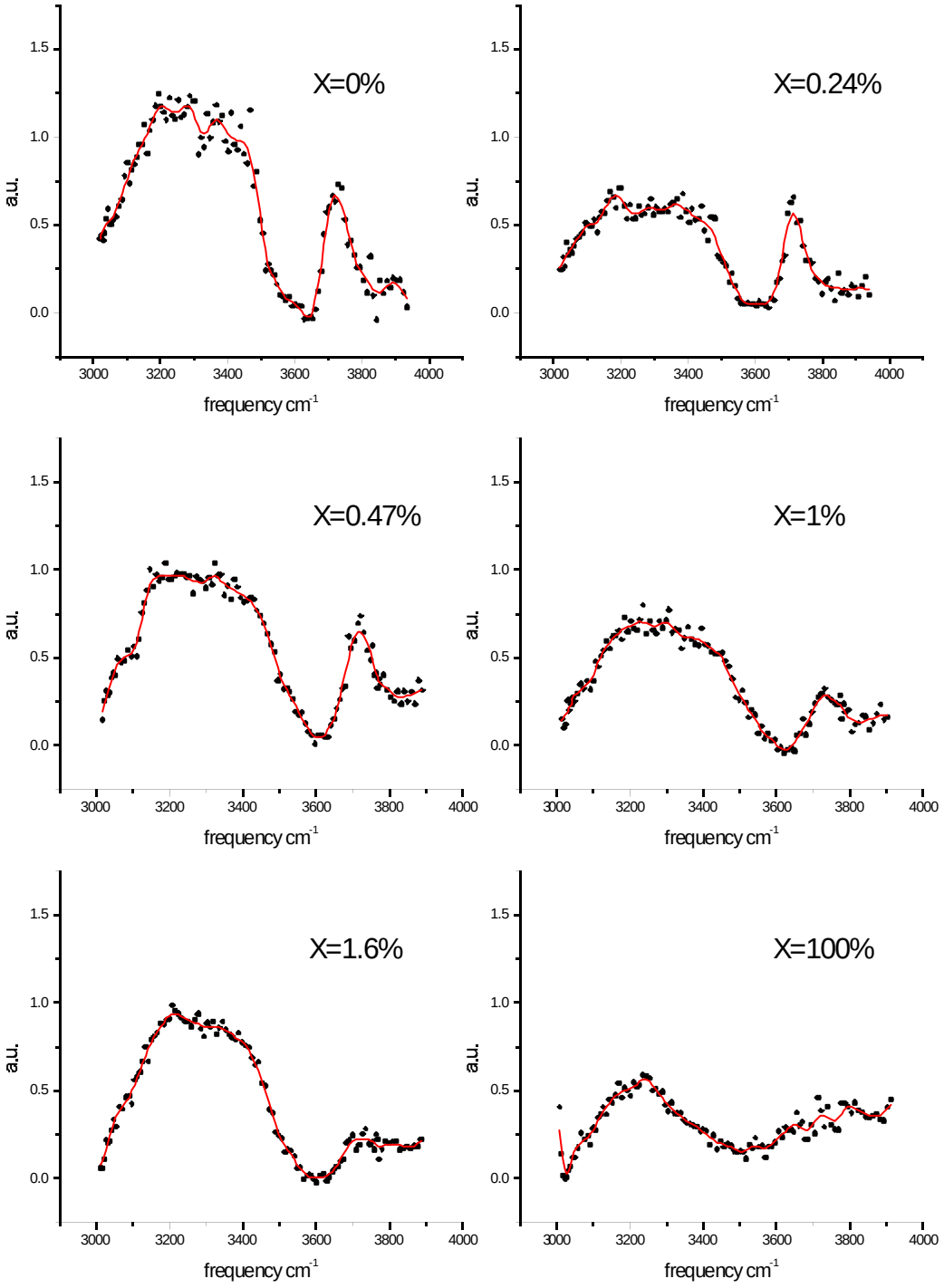

Fig. 1. Preliminary vibrational sum frequency generation spectra of the liquid/air interface for the system of ethanol:water solutions with various bulk concentrations of ethanol expressed in terms of molar ratio (x). ssp polarization combination is used for sum frequency, visible and infrared pulses, respectively. Solid curves are the results of five-point-smoothing through experimental data points.

Table 1. The Peak Position of the Free OH Stretch Versus the Ethanol Bulk Concentration

Bulk molar ratio	Frequency in cm^{-1}
0%	3721
0.24%	3714
0.47%	3722
1%	3732
1.6%	3727

group is stick ing out of the so lu tion above the nom i nal surface plane, and only the hydroxyl group is im mersed. The sur face layer of the mix ture is con sid ered as a mixed monolayer. This is a **sin gle layer pic ture** with re spect to ei ther the al co hol or the wa ter mol e cules. It pre dicts that an 18% surface den sity of eth a nol at bulk x = 0.01 (1%), a 29% sur face den sity at x = 0.016, and a 50% den sity at x = 4.4%.

Iso therm II as sumes that the n-alkyl group is to tally im mersed in side the so lu tion un der the nom i nal sur face. In this case, the ethyl group goes as far as ap prox i mately two wa ter lay ers deep into the so lu tion. And the sur face layer can be con sid ered as a monolayer with re spect to al co hol only, and mean while a **dou ble layer** with re spect to wa ter mol ecules. This is ad dressed as the **dou ble wa ter layer pic ture**. It is based on the same sur face ten sion and ac tiv ity co ef fi cients mea sure ments, and there fore the same cal cu lated sur face excess for eth a nol as **Iso therm I**, only the ex tra num ber of water mol e cules are taken into ac count to cal cu late the to tal num ber of the sol ute and sol vent in the sur face layer. It predicts a 11% sur face den sity of eth a nol at bulk x = 0.010, a 19% den sity at x = 0.016 (1.6%) and a 50% sur face den sity at bulk x = 11%.

In the case of a meth a nol:wa ter so lu tion, the dif fer ence be tween the two iso therms is not ap pre cia ble, but when the n-alkyl chain length in creases, the num ber of wa ter mol ecules that in ter act with the alkyl chain in creases, too. Thus arises the dis crep ancy.

Both mod els agree that the sur face eth a nol stands perpen dic u lar to the nom i nal sur face, with -OH fac ing the bulk, while the $-CH_3$ is fac ing the air. This agrees with Klein's obser va tion from his cal cu lated sur face struc ture for eth a nol: wa ter so lu tion that the ethyl group points out of the so lution.[13]

At bulk x = 0.010, **iso therm II** pre dicts a sur face density of 11%, while **iso therm I** pre dicts that of 18% for eth a nol. In ei ther case there should still be ap pre cia ble in ten sity for free OH con trib uted from the re sid ual dan gling bond. And in deed it is so as the spec tra for x = 1.0% shows: the sharp feature does not van ish into back ground.

At bulk x = 0.016, **iso therm II** pre dicts a sur face density of 19% for eth a nol, while **iso therm I** pre dicts that of 29%. If **iso therm I** is based on a more re al is tic model than **iso therm II**, then the free OH peak should be de pleted to nearly back ground at this con cen tra tion, and vice versa. And in deed we ob serve a very flat, if any, fea ture at this con cen tration. We thus con clude that in stead of the whole eth a nol mole cule, only the OH bond is im mersed in the mix ture so lu tion. And the sin gle (wa ter) layer pic ture should pre vail, ex clud ing the dou ble wa ter layer pic ture.

Al though the sharp fea ture due to free OH has dis appeared for the bulk con cen tra tion x = 1.6% and above (we have checked 5%, 14%, 20%) and turned into flat, pla teau like fea ture, we can still de tect the de crease of the SFG sig nal from the PMT as we block the in fra red beam unto the sam ple sur face. Al though the res o nant con tri bu tion to $\chi^{(2)}$ has turned into a non-resonant part, the pop u la tion of those once free OH has not just van ished. They should be now hy dro gen - bonded to OH of the eth a nol mol e cules, the en vi ron ment be ing inhomo geneous; there fore the once sharp fea ture has spread itself into a broad ened one.

With the el e va tion of eth a nol bulk con cen tra tion, the broad wa ter fea ture at 3200, 3400 cm^{-1} due to sur face wa ter mol e cules that are hy dro gen-bonded among each other does not seem to change much ex cept at x = 0.0024 (0.24%). The eth a nol added into the pure wa ter could in deed at tack the free OH first, leav ing the ice-like or dered struc tures alone for etha nol con cen tra tion be low x = 1.6%. But for the con cen tra tion higher than 1.6% and be low 20% in our work, with all of the 25% free OH been taken, we could not rule out the pos si bil ity that the ex cess eth a nol might start to in ter act with those wa ter mol e cules that are in the ice-like struc tures. The in ten sity of the or dered struc ture does not seem to change dra mat i cally, but the broad 3200 to 3400 cm^{-1} fea tures grad u ally grow narrow, re sem bling more and more those for the neat eth a nol. The low er ing of the or dered struc tures in ten sity at 0.24% might be as so ci ated with the on set of seg re ga tion of sur face eth a nol at 0.18%. Could the seg re ga tion take place at the expense of tum bling down part of the or dered struc ture? This re mains to be solved in fu ture work.

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REFERENCES

1. Shen, Y. R. *Nature* **1989**, *337*, 519.
2. Mizrahi, V.; Sipe, J. E. *Phys. Rev. B* **1986**, *34*, 3700.
3. Miranda, P. B.; Shen, Y. R. *J. Phys. Chem.* **1999**, *103*, 3292.
4. Super fine, R.; Huang, J. Y.; Shen, Y. R. *Phys. Rev. Let ters* **1991**, *66*, 1066.
5. Yeh, Y. L.; Zhang, C.; Held, H.; Mebel, A. M.; Wei, X.; Lin, S. H.; Shen, Y. R. *J. Chem. Phys.* **2001,** *114*, 1837.
6. Du, Q.; Freysz, E.; Shen, Y. R. *Science* **1994**, *264*, 826.
7. Shultz, M. J.; Schnitzer, C.; Simonelli, D.; Baldlli, S. *Int. Rev. in Phys. Chem.* **2000**, *19*, 123.
8. Brown, M. G.; Ray mond, E. A.; Al len, H. C.; Scatena, L. F.; Rich mond, G. L. *J. Phys. Chem. A* **2000**, *104*, 10220.
9. Stanners, C. D.; Du, Q.; Chin, R. P.; Cremer, P.; Somorjai, G. A.; Shen, Y. R. *Chem. Phys. Let ters* **1995**, *232*, 407.
10. Kipling, J. J. *J. Colloid Sci.* **1963**, *18*, 502.
11. Huang, J. Y.; Wu, M. H. *Phys. Rev. E* **1994**, *50*, 3737.
12. Wolfrum, K.; Graener, H.; Laubereau, A. *Chem. Phys. Letters* **1993**, *213*, 41.
13. Tarek, M.; Tobias, D. J.; Klein, M. C. *J. Chem. Soc. Far a-day Trans.* **1996**, *92*, 559.
14. Benjamin, I. *J. Chem. Phys.* **1999**, *110*, 8070.
15. Li, Z. X.; Lu, J. R.; Styrkas, D. A; Thomas, R. K.; Ren nie, A. R.; Penfold, J. *Mol. Phys.* **1993**, *80*, 925.
16. Vazquez, G.; Alvarez, E.; Navaza, J. M. *J. Chem. Eng. Data* **1995**, *40*, 611.
17. Glinski, J.; Chavepeyer, G.; Platten, J. K.; Smet, P. *J. Chem. Phys.* **1998**, *109*, 5050.
18. Lavi, P.; Mormur, A. *J. Colloid In ter face Sci.* **2000**, *230*, 107.
19. Huang, J. Y.; Shen, Y. R. In *La ser Spectrosopy and Photo chem is try on Metal Surfaces*; Dai, H. L.; Ho, W., Eds.; World Sci en tific: Sin ga pore, 1995; Adv. Ser. Phys. Chem. Vol. 5, Chap ter 1.