Interfacial Molecular Organization at Aqueous Solution Surfaces of Atmospherically Relevant Dimethyl Sulfoxide and Methanesulfonic Acid Using Sum Frequency Spectroscopy and Molecular Dynamics Simulation

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The molecular organization at the aqueous dimethyl sulfoxide (DMSO) and methanesulfonic acid (MSA) surfaces was investigated using vibrational sum frequency generation (VSFG) spectroscopy and molecular dynamics (MD) simulation. The molecular orientation of surface DMSO and MSA is deduced based on the VSFG spectra of both C–H stretch and S–O stretch regions. The S–O stretch region was studied for the first time and is shown to be critical in molecular orientation determination. On average, the CH3 groups of DMSO and MSA are preferentially pointing outward into the air. However, the DMSO S==O group points slightly inward away from the surface, while the SO3 vector of dissociated MSA points nearly straight down. In addition, MD simulations reveal that the orientation distribution of surface DMSO is relatively broad in contrast with a narrow distribution of surface MSA, which agrees with the experiment findings.

Introduction

Organosulfur compounds of both natural and anthropogenic origin have been found to be involved in many reactions taking place at the aerosol surface.1 In the marine boundary layer (MBL), the sulfur cycle dominates in the gas to particle conversion process and in the growth of aerosols.2 Tropospheric sulfur-containing aerosols play an important role in climate as well as in related heterogeneous atmospheric chemical processes.3,4 A significant sulfur source in the MBL is the biogenic dimethyl sulfide (DMS) produced by metabolic processes of algae.5,6 Because of its high volatility and reactivity, DMS is easily oxidized in the atmosphere and produces many stable intermediates such as dimethyl sulfoxide (DMSO, (CH3)2S==O) and methanesulfonic acid (MSA, CH3==SO2==OH).7,8 Oxidation of DMSO, MSA, and other intermediates can take place at the aerosol surface and in the bulk of the aerosol through reactions with OH radicals, which eventually leads to the formation of H2SO4.9 The sulfur-containing aerosols serve as cloud condensation nuclei, influencing the formation of clouds and thereby modifying the earth’s albedo.3,4,10 Therefore, the uptake of organosulfur species and the molecular organization at the aerosol surface are of great interest in atmospheric chemistry.

Besides the important atmospheric implications, DMSO, MSA, and their aqueous solutions also have a wide range of applications in other chemical processes. In organic chemistry, DMSO is among the most widely used solvents.11 Biological properties of DMSO are also important. Due to its amphiplic nature, DMSO interacts strongly with molecules in cell membranes, which promotes membrane permeability12,13 and induces cell differentiation14 and fusion.15 Because of its strong interaction with water, aqueous DMSO solutions display strong nonideal behavior. For example, they can reach freezing points near the temperature of liquid nitrogen, and, therefore, can be used as a cryoprotectant for biological structures such as tissues and proteins.16 Methanesulfonic acid, similar to DMSO, is completely miscible with water at any concentration. Moreover, MSA is a strong acid (pKa = −1.9) and is widely used as an acid electrolyte in many electrochemical processes.17

Extensive efforts have been made to elucidate molecular organization in the bulk solutions of aqueous DMSO and MSA.18–23 In particular, DMSO–water mixtures have been investigated by a wide variety of experimental techniques such as X-ray and neutron diffraction,21,24 infrared (IR) and Raman spectroscopy,25,26 nuclear magnetic resonance (NMR),27,28 and acoustic spectroscopy29 as well as computer simulations.18–20,30 These studies led to the conclusion that DMSO as a hydrogen bond acceptor forms strong hydrogen bonds with water molecules. The hydrogen bond between DMSO and water is even more pronounced than that between water molecules.21 The methyl groups of DMSO, although hydrophobic, are loosely hydrated by surrounding water molecules.22 Similar hydrogen-bonding ability of MSA with water is observed due to the S–O moieties.23

Because of the noticeable surface preference of DMSO and MSA,31–33 the structure and properties of the surface of their aqueous solutions are also of interest. In contrast with the relatively abundant bulk information, the molecular organization at the surface is still not well understood due to limited surface-specific techniques for aqueous media. Only nonlinear spectroscopic methods such as second harmonic generation (SHG)34 and vibrational sum frequency generation (VSFG) have been utilized to study the surface of aqueous solutions of DMSO and

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A concentration VSFG study of aqueous DMSO showed that the square root of the CH_{3} intensity was proportional to the determined surface DMSO number density, which suggested that the average orientation of DMSO CH_{3} groups remains unchanged with different mixing ratios with water. However, the actual orientation of DMSO at the surface has not been reported.\textsuperscript{35} In addition, a VSFG study calculated the polarization combinations of incident visible and IR pulses such as ssp, sps, and psp, where the three polarizations refer to the polarization of sum frequency light, visible light, and IR light in order. For instance, ssp means s-polarized output sum frequency signal with s-polarized incident visible and p-polarized incident IR pulses.

In different polarization combinations the effective second-order susceptibility, \(\chi^{(2)}_{\text{eff}}\) is related to the macroscopic second-order susceptibility \(\chi^{(2)}_{\text{m}}\) as shown in eqs 2 and 3:\textsuperscript{41}

\[
\chi^{(2)}_{\text{eff,ssp}}(\omega) = L_{\gamma\gamma}(\omega) L_{\gamma\gamma}(\omega) L_{zz}(\omega_{\text{IR}}) \sin \theta_{\text{IR}} \chi_{\gamma\gamma \gamma \gamma}^{(2)}
\]

\[
\chi^{(2)}_{\text{eff,ppp}}(\omega) = -L_{\gamma\gamma}(\omega) L_{\gamma\gamma}(\omega) L_{zz}(\omega_{\text{IR}}) \cos \theta_{\text{IR}} \sin \theta_{\text{IR}} \chi_{zzzz}^{(2)}
\]

Thus, a general but not complete picture of the surface of aqueous solutions of DMSO and MSA including the surface concentration, molecular interactions and orientation, and interfacial water structure has been presented.

In this paper, the VSFG technique with complementary infrared (IR) and Raman spectroscopies are employed to present a comprehensive study of the liquid/vapor interface of aqueous solutions of DMSO and MSA to elucidate the molecular organization and orientation, and intermolecular interactions. Taking advantage of the ability to probe in the low-frequency vibrational region (fingerprint region), the S-O moieties in DMSO and MSA are investigated here for the first time for these molecules. In concert, molecular dynamics (MD) simulations are performed to gain more insight on the experimental results.

### Experimental Section

**Materials.** DMSO and methanesulfonic acid (>99% purity) were purchased from Fisher. 1,2-Dipalmitoyl-sn-glycero-3-phosphate (DPPA) was obtained from Avanti Polar Lipids (Alabaster, AL). Deionized water (not purged of CO\textsubscript{2}) with a resistivity of 18.2 M\textOmega\cdot cm and a measured pH of 5.5 was from a Barnstead Nanopure system. Concentrations are reported in units of mole fraction denoted as \(x\).

**VSFG Spectroscopy.** The broad bandwidth VSFG system\textsuperscript{30,40} consists of two 1 kHz repetition rate regenerative amplifiers (Spectra-Physics Spitfire, femtosecond and picosecond versions), both of which are seeded by sub-50 fs 792 nm pulses (the wavelength is tuned for system optimization) from a Ti:sapphire oscillator (Spectra-Physics, Tsunami) and pumped by a 527 nm beam from an all solid-state Nd:YLF laser (Spectra-Physics, Evolution 34). The two regenerative amplifiers provide 85 fs pulses and 2 ps pulses at 792 nm. The spectrally broad femtosecond pulses are used to drive the infrared generation in an OPA (optical parametric amplifier; TOPAS, Quantronix) and then produce broad bandwidth infrared pulses (~200 cm\textsuperscript{-1} fwhm). Stable infrared pulses are tunable in various wavelength ranges ranging from 1000 to 3800 cm\textsuperscript{-1}. At the sample stage, the incident angles of visible and IR are 53\textdegree and 68\textdegree, respectively, the energy of the 792 nm picosecond pulse was set to 300 \(\mu\text{J}\), and the IR femtosecond pulse was ~9 \(\mu\text{J}\) in the C–H stretching region and ~3 \(\mu\text{J}\) in the S–O stretching region.

The intensity of the reflected sum frequency signal, \(I_{\text{SFG}}\), is proportional to the absolute square of the effective second-order susceptibility, \(\chi^{(2)}_{\text{eff}}\), and to the visible and IR pulse intensities as shown in eq 1:\textsuperscript{41}

\[
I_{\text{SFG}} \propto |\chi^{(2)}_{\text{eff}}|^2 I_{\text{vis}} I_{\text{IR}}
\]

VSFG experiments can be conducted with a variety of polarization combinations of incident visible and IR pulses such as ssp, sps, and psp, where the three polarizations refer to the polarization of sum frequency light, visible light, and IR light in order. For instance, ssp means s-polarized output sum frequency signal with s-polarized incident visible and p-polarized incident IR pulses.

In different polarization combinations the effective second-order susceptibility, \(\chi^{(2)}_{\text{eff}}\) is related to the macroscopic second-order susceptibility \(\chi^{(2)}_{\text{m}}\) as shown in eqs 2 and 3:\textsuperscript{41}

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\]

\[
\chi^{(2)}_{\text{eff,ppp}}(\omega) = -L_{\gamma\gamma}(\omega) L_{\gamma\gamma}(\omega) L_{zz}(\omega_{\text{IR}}) \cos \theta_{\text{IR}} \sin \theta_{\text{IR}} \chi_{zzzz}^{(2)}
\]

where \(\theta_{i}\) is the angle of the indicated light to the surface normal and \(L(\omega)\) is the Fresnel factor (see Supporting Information).

**Molecular Orientational Analysis.** The capability of quantitative determination of molecular orientation is a significant advantage of VSFG technique compared to other spectroscopic methods. The macroscopic second-order susceptibility \(\chi^{(2)}_{\text{m}}\) is related to the microscopic molecular hyperpolarizability \(\beta(2)\) through average molecular orientation. For the symmetric stretch (SS) of C\(_{60}\) groups discussed in this paper, the nonvanishing \(\beta(2)\) are \(\beta_{ssc} = \beta_{bc} = \beta_{cc}\).\textsuperscript{42} The relationship between \(\chi^{(2)}_{\text{m}}\) and \(\beta(2)\) through can be expressed as shown in eqs 4–6:\textsuperscript{41–43}

\[
\chi_{\gamma\gamma \gamma \gamma}^{(2)} = \frac{1}{2} N \beta_{ssc} (\cos \theta - \cos^3 \theta)(1 - R)
\]

\[
\chi_{zzzz}^{(2)} = \frac{1}{2} N \beta_{ssc} (\cos \theta - \cos^3 \theta)(1 - R)
\]

\[
\chi_{zzzz}^{(2)} = \frac{1}{2} N \beta_{ssc} (\cos \theta + \cos^3 \theta)(1 - R)
\]
\[ \rho = \frac{3}{4 + 5\left(\frac{2R + 1}{R - 1}\right)^2} \]  

(7)

where \( \rho \) is the ratio of the Raman intensities with polarization perpendicular and parallel to the excitation light. This is measured by the polarized Raman experiment shown in eq 8:

\[ \rho = \frac{I_\perp}{I_\parallel} \]  

(8)

Only one of the retrieved R values from solving the quadratic equation is physically correct,\(^{46}\) which can be validated from a polarized VSFG experiment. For molecular groups with \( C_{3v} \) symmetry, the value of \( R > 1 \) is a simple check from the bond additive model.\(^{42}\)

However, sometimes the VSFG intensity of a specific polarization combination could be very low (for example, the ppm spectrum of DMSO CH, is more than 10-fold lower in intensity than the ssp spectrum), which as a result leads to large experimental errors in orientation analysis from a quantitative aspect. The polarization null angle method, as shown in the literature,\(^{43,47}\) can improve the accuracy of the measured ratio of effective second-order susceptibilities \( \chi^{(2)} \) and hence accuracy of the determined orientation angle. A detailed description of the polarization null angle method is in the Supporting Information.

Computer Simulations. MD simulations of DMSO or MSA in an aqueous slab were performed. We used a unit cell containing 863 water molecules and 16 DMSO or MSA molecules (corresponding roughly to 1 M (0.02 \( x \)). The size of the prismatic unit cell was \( 30 \times 30 \times 100 \) Å and 3D periodic boundary conditions were applied.\(^{46}\) We used a 12 Å cutoff for intermolecular interactions. Long-range Coulomb interactions were accounted for using the particle mesh Ewald procedure.\(^{49}\) Simulations were run in the NTV canonical ensemble at 300 K. A time step of 1 fs was employed, and all bonds involving hydrogen atoms were constrained using the SHAKE algorithm.\(^{50}\) All systems were first equilibrated for 500 ps, after which a 1 ns production run followed.

A polarizable force field was employed. For water, we used the POL3\(^{51}\) water model. For DMSO or MSA we used the general amber force field parameter set.\(^{52}\) Partial charges were evaluated using the standard RESP procedure employing the Gaussian 03 program\(^{53}\) and all MD simulations were performed using the Amber 8 program.\(^{54}\)

Results and Discussion

DMSO at the Surface. DMSO–water mixtures have been investigated by various spectroscopic methods including IR, Raman, and VSFG. The S=O moiety is the key part which accounts for the dipolar interactions of DMSO. Figure 1 shows the Raman spectra in the S=O stretch region of a series of DMSO–water mixtures. The peak near 950 cm\(^{-1}\) is assigned to a rocking mode of DMSO CH\(_3\).\(^{55}\) For pure DMSO, a broad band peaked at 1043 cm\(^{-1}\) is observed for the S=O stretch mode.\(^{26}\) The asymmetric band shape ranges from 1000 to 1100 cm\(^{-1}\) and has a shoulder at \( \sim 1055 \) cm\(^{-1}\). This broad shape of S=O stretch shows the existence of different aggregates in pure DMSO. The S=O frequency of DMSO monomer as diluted in carbon tetrachloride was found to be around 1070 cm\(^{-1}\).\(^{55}\) Because of the negligible interaction between CCl\(_4\) and the DMSO S=O group, this frequency is considered to be unperturbed. In pure DMSO, a strong dipolar interaction was identified between DMSO molecules, leading to formation of DMSO dimers and chain aggregates.\(^{26,38}\) Therefore, the peak at 1043 cm\(^{-1}\) is assigned to the symmetric stretch of the cyclic DMSO dimer.\(^{26}\) As the water content increases in the DMSO–water mixtures, a clear red shift in the S=O stretch frequency is observed, which is generally attributed to the DMSO–water interaction. The concentration dependence of the S=O frequency red shift was proposed to be correlated with a cluster model (DMSO\(_x\)(H\(_2\)O)\(_y\)). When \( x \gg y \), as in nearly pure DMSO, the dipolar interaction between DMSO molecules dominates. On the other hand, hydrogen bonding between DMSO and water molecules is more pronounced when \( y \gg x \). At 0.66 x DMSO the peak intensity at 1030 cm\(^{-1}\) is about the same as that at 1043 cm\(^{-1}\), which indicates the coexistence of DMSO in different chemical environments. Previous MD simulation also suggested the tendency of DMSO and water to preserve their own structural order upon mixing.\(^{18}\) In rather dilute DMSO solutions (<0.33 \( x \)) the width of the S=O stretch band becomes narrower, suggesting a more similar or homogeneous environment for DMSO. No significant red shift is found between the 0.1 \( x \) and 0.02 \( x \) DMSO solution spectra, both showing the S=O frequency centered at 1012 cm\(^{-1}\).

Although IR activity of the DMSO S=O stretch is also observed (data not shown), VSFG of the DMSO S=O stretch has not been reported so far. Indeed no VSFG intensity in the S=O stretch region is detected for the 0.1 \( x \) DMSO in the ssp polarization combination as shown in Figure 2. VSFG intensity not only relates to the molecular hyperpolarizability but also to the molecular orientation at the surface and therefore lack of ssp polarization signal could indicate surface disordered DMSO molecules or orientation of the S=O near the plane of the surface. However, the significant VSFG intensity of DMSO methyl groups, discussed below, indicates that disorder is not the reason for lack of VSFG signal. Previous MD simulations have predicted the orientation of the S=O vector at the surface of both neat DMSO\(^{38}\) and aqueous DMSO solutions.\(^{36}\) The S=O vector orientation of the top layer of molecules was found to be parallel to the surface of neat DMSO, while at the aqueous DMSO (<0.2 \( x \)) surface, the average S=O vector orientation was predicted to be \( \sim 30^\circ \) away from the surface plane. Both theoretical results suggest that the S=O vector in DMSO prefers to orient close to the surface, which as a consequence, leads to a vanishing of the ssp VSFG intensity.
After spreading of negatively charged phospholipid DPPA onto the 0.1 x DMSO solution, two broad peaks centered at ∼1012 and ∼1120 cm$^{-1}$ are observed. The higher frequency peak is the DPPA PO$_2^-$ stretch as shown in Figure 2. The agreement of the 1012 cm$^{-1}$ DMSO peak position with Raman spectra further proves that the lower frequency 1012 cm$^{-1}$ peak is the S$\delta$O stretch of DMSO. This result clearly shows that the S$\delta$O vector orientation is affected by the local electric field created by the negative charge of the DPPA headgroup at surface; namely, the S$\delta$O vector is more perpendicular to the surface with the oxygen pointing to the bulk as shown in Scheme 1. This result indicates that an applied field can orient the S$\delta$O and that this orientation can be detected. This result still does not clarify the S═O orientation at the surface of an aqueous solution, but at the least, it excludes the possibility of a rather straight down conformation of the S═O bond.

For DMSO, the two CH$_3$ groups are in a fixed molecular geometry, ∠C$\cdash$S$\cdash$C = 97.4°, and the angle between the S═O bond and the C$\cdash$S$\cdash$C plane is 64°. However, the tilt angles of the CH$_3$ groups to the surface normal are determined by the angle between the surface normal and the C$\cdash$S$\cdash$C plane. Without knowing the angle between the surface normal and the C$\cdash$S$\cdash$C plane, retrieval of DMSO CH$_3$ orientation angle is not unique. Here we assume the C$\cdash$S$\cdash$C plane of DMSO to be perpendicular to the liquid surface, which leaves the S$\delta$O vector to be ∼26° buried close to the surface as suggested by the MD simulation and our VSFG S$\delta$O result. The VSFG spectra in the C$\cdash$H stretch region of 0.2 x DMSO is shown in Figure 3. In ssp polarization the peak centered at 2913 cm$^{-1}$ is the CH$_3$ symmetric stretch. Single peak has contribution from both CH$_3$ groups. The VSFG frequency of the DMSO CH$_3$ symmetric stretch blue shifts as the DMSO concentration decreases (data not shown) which is in accordance with previous literature. This blue shift is also observed in a bulk infrared study and is attributed to the effect of the hydration of the CH$_3$ groups as explained by the pushball mechanism. In addition, a previous VSFG concentration study on aqueous DMSO suggested that the orientation of DMSO methyl groups remains relatively unchanged at all mixing ratios with water although no orientation value was given. Based on this, only one aqueous DMSO concentration is used to investigate the DMSO orientation at the air/water interface in the present study.

Usually, the VSFG intensity ratios of different polarization combinations, i.e., ssp, ppp, or sps, are used to determine the average orientation of the specified group. This method is convenient when appreciable VSFG intensities can be measured in these polarization combinations. For the DMSO CH$_3$ groups, although there is decent intensity in ssp polarization, intensity in ppp polarization (data not shown) is more than 1 order of magnitude less than in ssp polarization. Using the VSFG intensity ratio to determine the DMSO CH$_3$ orientation could therefore be subject to a relatively large error. In this case, the CH$_3$ orientation can be more accurately determined through polarization null angle analysis as demonstrated in previous studies. In our experiment, the polarization of IR is fixed at p while the polarization of visible is set to −45° (equal mixing of s and p), so that both ssp and ppp VSFG signals can be detected. If the detection polarization angle for VSFG is set to s, only half of the intensity will be observed as shown in Figure 3. A certain detection polarization angle (so-called null angle)
can be measured at which the total output VSFG intensity vanishes. For 0.2 M DMSO CH$_3$ groups, the null angle is determined to be $-10.8^\circ \pm 2.0^\circ$ as shown in the inset of Figure 3, which corresponds to the $\chi_{CH_{ppp}}^{eff}/\chi_{CH_{isp}}^{eff}$ of $-0.191 \pm 0.036$.

In addition, the value of the hyperpolarizability ratio ($R$) of DMSO CH$_3$ groups is required. Because the CH$_3$ groups are related through the assumed molecular geometry, $R$ can be related to the orientation angle through the VSFG study of acetone CH$_3$ groups at the vapor/acetone interface.$^{56}$ Using the values above, the two tilt angles are determined to be $90^\circ$, although it is clear that the overall probability between 0$^\circ$ and 180$^\circ$ is lower. The difference between the spectra of 0.02 M DMSO CH$_3$ and pure MSA is marked. A sharp peak at 1050 cm$^{-1}$ is observed at low MSA.

The two CH$_3$ groups could have different tilt angles, which can be related through the assumed molecular geometry: $\theta_1 = 97.4^\circ - \theta_2$. Similar treatment was also employed in previous VSFG study of acetone CH$_3$ groups at the vapor/acetone interface.$^{56}$ Using the values above, the two tilt angles are determined from eqs 2-6 to be $27.0^\circ \pm 4.0^\circ$ and $70.4^\circ \pm 4.0^\circ$, respectively. This indicates that, on average, while assuming that the two CH$_3$ groups point toward the air phase, DMSO molecules are only slightly tilted from the surface normal at the surface. However, the above tilt angles of DMSO CH$_3$ groups are the average values retrieved using a $\delta$-distribution assumption. The orientation parameter $D$ retrieved in our experiment is 1.65 (the value at the magic angle is 1.66), which indicates that the DMSO CH$_3$ groups could orientate at other average tilt angles, but with relatively broad distributions,$^{54}$ although from the relatively strong CH$_3$ VSFG signal, at least the partial ordering of DMSO molecules at the surface is anticipated.

Orientations of DMSO molecules have been also simulated using MD simulations of 1 M DMSO in an aqueous slab. A representative snapshot from the simulation (Figure 4) provides a qualitative flavor of the distribution of DMSO across the slab and about their interfacial orientations. Quantitatively, the density distribution of DMSO molecules averaged over the whole simulation shows the surface activity of this molecule (Figure 5). Results concerning the orientational preference of DMSO are quantified in Figure 6. The $x$-axis is the orientation angle between the DMSO molecular axis (passing through the carbon and sulfur) and the outward surface normal. A broad distribution of probability is observed for the orientation angle, although it is clear that the overall probability between 0$^\circ$ and 90$^\circ$ is higher than between 90$^\circ$ and 180$^\circ$, confirming that on average DMSO CH$_3$ groups are pointing outward into the air phase. This broad distribution is within the regime as suggested by the value of the determined orientational parameter $D$. In addition, the maximum probability is found at around 20$^\circ$ with a secondary weak maximum around 70$^\circ$, supporting the experimental finding of $27.0^\circ \pm 4.0^\circ$ and $70.4^\circ \pm 4.0^\circ$ respectively. In that case, the absolute orientation of the $S=O$ bond is determined by rotating the C$-$S$-$C plane about the C$-$S$-$C plane normal to meet with the orientation of the CH$_3$ groups as shown in a previous VSFG study.$^{57}$ From the fact that the angle between the S=O bond and the C$-$S$-$C plane is 64$^\circ$, the tilt angle of the S=O bond to the surface normal obtained is 66$^\circ$ ($\sim$ 24$^\circ$ buried close to the surface). Hence, in addition to the ordering of the DMSO methyl groups as shown here experimentally and supported by MD simulation, it is concluded that the S=O bond of DMSO is also not disordered, and lies close to the aqueous DMSO solution surface in agreement with a previously reported MD result of the S=O.$^{36}$

**MSA at the Surface.** Unlike DMSO which can only accept hydrogen bonds, MSA is both a hydrogen bond donor and acceptor. The Raman spectra of aqueous MSA in S$-$O stretch region are shown in Figure 7. The spectra reveal the sensitivity of the MSA S$-$O bond frequency to hydration and deprotonation. The difference between the spectra of 0.02 M and pure MSA is marked. A sharp peak at 1050 cm$^{-1}$ is observed at low MSA.
concentration, which is assigned to the SO$_3$\textsuperscript{-} symmetric stretch in the dissociated form.\textsuperscript{58} The spectral pattern remains up to 0.1 x MSA concentration, which is in agreement with the over 90% ionization degree of MSA at this concentration as reported in the literature.\textsuperscript{58} When the molar ratio of MSA:water is 1:1, undissociated MSA is observed to be dominant. Meanwhile the SO$_3$\textsuperscript{-} peak intensity decreases significantly as concentration goes up. The peak at 1126 cm\textsuperscript{-1} and the shoulder around 1174 cm\textsuperscript{-1} are assigned to the bending mode of undissociated S–O–H and the SO$_2$ symmetric stretch respectively, as suggested by previous studies.\textsuperscript{22,58} Molecular MSA can easily form hydrogen bonds with water and itself.\textsuperscript{22} In pure MSA, self-association to form cyclic dimers should prevail, while a 1:1 MSA–water complex exists in a 0.5 x MSA solution. However, the Raman peak positions and intensities of the S–O–H bend and SO$_2$ symmetric stretch are almost identical for pure and 0.5 x MSA regardless of the fact that they are different species. This suggests that the hydrogen bonds formed between MSA molecules and between MSA and water molecules are similar.

Orientation of MSA molecules at the surface is reasonably different for its molecular and ionized forms. At low concentrations (<0.1 x), MSA molecules dissociate almost completely and the anion has two coaxial C$_3$V groups, the CH$_3$ and SO$_3$\textsuperscript{-}. Therefore, the molecular orientation can be determined from the orientation of either the CH$_3$ or SO$_3$\textsuperscript{-} groups.

The VSFG spectra of 0.1 x aqueous MSA in both C–H stretch and S–O stretch regions are shown in Figure 8. In the C–H stretch region the sharp peak observed at 2944 cm\textsuperscript{-1} is from the symmetric stretch of the CH$_3$ group. The negative interference feature around 3030 cm\textsuperscript{-1} is the position of the CH$_3$ asymmetric stretch. The apparent peak positions are not the exact peak positions of the component peaks due to interference of adjacent resonances. In addition, the broad proton continuum intensity is clearly seen to extend down below 2800 cm\textsuperscript{-1}. The VSFG intensities in ppp and sps polarizations, however, are nearly undetectable, which is in accordance with previous reports.\textsuperscript{33} Therefore, it is not possible to accurately measure the CH$_3$ orientation based on such low spectral intensities. In contrast, the VSFG intensities of the SO$_3$\textsuperscript{-} group in both sps and ppp polarizations can be collected with relatively good signal-to-noise ratios as shown in Figure 8. A single peak at 1050 cm\textsuperscript{-1} in the VSFG spectra indicates that the surface moiety probed at this concentration is still the SO$_3$\textsuperscript{-} group even though molecular MSA may also exist at the surface. Similarly the Raman depolarization ratio $\rho$(SO$_3$\textsuperscript{-}) is measured to be 0.039 $\pm$ 0.001 from a polarized Raman experiment (Supporting Information), which then gives the hyperpolarizability ratio $R$(SO$_3$\textsuperscript{-}) of 2.65 $\pm$ 0.05. Therefore, based on the measured intensity ratio of sps/ppp and the $R$(SO$_3$\textsuperscript{-}) above, the average tilt angle of SO$_3$\textsuperscript{-} group can be determined from eqs 2–6 to be 16.0° $\pm$ 2.0°, indicating a relatively straight up conformation of MSA, aligned with the surface normal.
where the probability value peaks at 5°, which is in accordance with the straight up conformation deduced from experiment results despite that the concentrations in experiment and simulation are slightly different (although both are performed in water-rich solutions).

Conclusions

A comprehensive investigation of the molecular organization at aqueous DMSO and MSA surfaces has been completed using VSFG spectroscopy and MD simulations. For DMSO molecules at the aqueous surface, the orientation has a relatively broad distribution, but preferentially with the two CH₃ groups pointing outward into the air. On average, the two DMSO CH₃ groups are tilted at the surface, with tilt angles of ~27° and ~70°, respectively. The S=O group is hydrated by the aqueous phase and points only slightly inward to the interior of the solution. MSA molecules completely dissociate into hydrated ions at low concentrations (<0.1 M). Deprotonated MSA (methanesulfonate anions) reside at the surface in a relatively straight up conformation with their SO₃ vector pointing inward and their CH₃ vector pointing outward, with both moieties oriented ~16° from the surface normal in their residing phase, aqueous and gas, respectively.

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Supporting Information Available: Description of the polarization null angle mathematics, Fresnel coefficients, refractive indices used for SFG orientation calculations, and Raman polarized spectra for MSA CH₃ and SO₃⁻ modes. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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