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Non-linear vibrational sum frequency spectroscopy of atmospherically relevant molecules at aqueous solution surfaces

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Abstract

Surface vibrational sum frequency spectroscopy has been shown to be a powerful surface probe of molecules adsorbed at solid and liquid surfaces. Studies described herein apply this method to studying heterogeneous air/aqueous solution interfaces to understand surface adsorption and structure of several solute molecules adsorbed at aqueous surfaces. The molecules examined at aqueous solution surfaces include dimethyl sulfoxide (DMSO), methane sulfonic acid (MSA) and acetone. These results reveal that small soluble molecules such as these organize in different ways at the surface of aqueous solutions. This surface organization has implications for atmospheric chemical processes since adsorption at the surface of atmospheric aerosols affects bulk chemical concentrations. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Vibrational sum frequency spectroscopy (VSFS); Air-water interface; Dimethyl sulfoxide (DMSO); Methane sulfonic acid (MSA)

1. Introduction

The chemistry of the atmosphere involves both homogeneous and heterogeneous processes. Whereas atmospheric molecules have been studied extensively in the gas phase, very few spectroscopic studies have investigated these molecules on liquid surfaces of environmental relevance. In this paper we discuss studies of the molecular structure of atmospherically important molecules at an aqueous surface completed by this research group [1–4]. Specifically, adsorption and structural information from surfaces of aqueous solutions of dimethyl sulfoxide, methane sulfonic acid and acetone are presented. These molecules are present as trace constituents in the atmosphere, and while water soluble have significant surface activities. Due to the abundance of water in the lower atmosphere, understanding the molecular interactions that occur at aerosol surfaces is of importance. Recently, dimethyl sulfoxide has been proposed as the heterogeneous precursor to atmospheric condensed phase MSA through an atmospheric cycle originating with dimethyl sulfide, a phytoplankton degradation product [5–7]. Aerosol particles containing MSA are thought to contribute to the class of aerosols which effectively scatter radiation out of the atmosphere [6,8]. Acetone, ubiquitous in many regions of the atmosphere, has recently been shown in regional studies in the North-

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ern Hemisphere to be the second highest concentration organic trace-gas constituent next to methane and may play a role in the growth and surface chemistry of atmospheric aerosols [9]. There has also been an ongoing effort to understand the atmospheric heterogeneous chemistry of acetone on condensed phase sulfuric acid [10]. The molecular similarities of these molecules also provide interesting comparisons for understanding molecular adsorption of solute molecules on aqueous surfaces in general.

Heterogeneous processes occurring at the gas/liquid interface are intrinsically difficult to study at the molecular level. The surface specific second-order non-linear optical technique of vibrational sum frequency spectroscopy (VSFS) has proved in the past 10 years to be a powerful method for making such measurements. Recent advances in this technique, including shorter pulses and novel methods for generating infrared radiation have made the weak signals generated by molecules at these types of interfaces accessible [11–13].

The theory of vibrational sum frequency spectroscopy (VSFS), has been extensively described previously [14–19], so only a brief description will be discussed here. VSFS probes only those molecules existing in an environment which lacks inversion symmetry, such as the air/water interface. The intensity of the generated sum frequency light, I_{SF}, is proportional to the square of the second-order macroscopic susceptibility, $\chi^{(2)}$:

$$I_{SF} \propto |\chi^{(2)}_{NR} + \chi^{(2)}_{R}|^2 I_{IR} I_{vis}, \tag{1}$$

where NR and R denote the non-resonant and resonant pieces of the second-order susceptibility, and I_{IR} and I_{vis} are the intensities of the incident infrared and visible pulses that give rise to the SF response. $\chi^{(2)}_{R}$ is proportional to the number of orientationally averaged molecules in the interfacial region and is resonantly enhanced when the incident infrared beam is resonant with vibrational modes of the interfacial molecules. Since the probability of producing a SF photon from the two incident pules (IR and visible) is low, improved detection techniques have been employed to improve the signal to noise levels.

All of the spectra shown are taken using a SSP polarization combination, where SSP denotes the polarization of the sum frequency, incident visible and incident infrared beams, respectively (S polarized light oscillates perpendicular to the plane of incidence, while P polarization is in the plane of incidence). This polarization combination probes the second-order susceptibility χ_{yyz}, which contains information on the resonant IR transition moments perpendicular to the surface and the isotropic Raman response. Thus the molecules in the interfacial region whose transition moment is perpendicular to the surface plane will significantly contribute to a SSP sum frequency spectrum.

Due to the coherent nature of the sum frequency process, the phase of the SF response must be included in the full analysis of the spectra to deconvolve the contributing interference effects [4,17,20,21]. It has been shown that under the SSP polarization condition, for vibrational modes of either C_{3v} or C_{2v} symmetry, the symmetric and asymmetric stretch modes will destructively interfere [20,22]. Recall that the SF intensity is the square of a sum of terms, thereby producing cross-terms in the expression for the SF intensity. These cross-terms produce dips and asymmetric peaks in the spectra that are not observed in conventional IR and Raman spectroscopies. In the studies discussed here, where the methyl vibrational modes are all of C_{3v} symmetry, a destructive interference is observed between the methyl symmetric and asymmetric stretch peaks.

2. Experimental

The laser system used for these VSFS experiments has been previously described in detail [2,11,12]. Briefly, two coherent beams (2-ps pulses at a kHz rep rate), one in the visible at 800 nm, the other tunable through the OH and CH stretching regions (2750–4000 cm^{-1}), are spatially and temporally overlapped on the solution surface. The resulting SF beam passes through a series of spatial and wavelength filters, and is focused onto a thermoelectrically cooled CCD camera. In addition to vastly improving the signal to noise ratio, the CCD array allows for more precise spatial positioning and characterization of the SF response. The recent improvements in the IR generation and the use of the CCD camera for detection have made possible the measurement of the inherently low SF response from small molecules at air–aqueous solution interfaces.

3. Results and discussion

The SSP VSF spectrum from the surface of a pure dimethyl sulfoxide solution has been measured [1] and is shown in Fig. 1. The large peak at 2914 cm^{-1} is assigned to the CH_3 symmetric stretches (SS) of DMSO. The CH_3 asymmetric stretches (AS) of the two methyl groups of DMSO are assigned to a peak at 2990 cm^{-1}. All frequencies from the VSF spectra have an associated uncertainty of ±5 cm^{-1}. The CH_3-AS assignment was taken from the fit to the spectrum, which is shown with the data in Fig. 1 and is broken down into composite peaks in Fig. 2. These

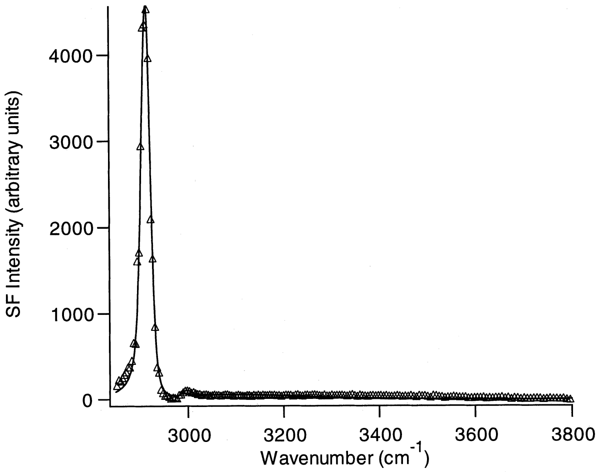

Fig. 1. SSP VSF spectrum of pure DMSO. The triangles represent data points, while the solid line is the best fit to the data. The fit includes the appropriate phase relationships between the contributing peaks.

frequencies are in close agreement with the frequencies found in bulk Raman and IR studies [23]. Due to improved laser and detection instrumentation, the frequency measured here for the CH_3-SS peak is somewhat different and more accurate than previously measured in this laboratory [1]. The asymmetry of the CH_3-SS peak, specifically the sharper SF intensity drop on the high energy side, and the following dip in the spectrum are attributed to the destructive interference between the CH_3-SS mode and the CH_3-AS mode. As expected, there are no other readily discernable features in either the CH stretching region or the higher energy region shown.

Fig. 2 shows more clearly the region assigned to the destructive interference between the CH_3-SS and the CH_3-AS, and the peaks which make up the fit to the spectrum shown in Fig. 1. The large intensity of the symmetric stretch relative to the asymmetric stretch indicates that the methyl groups are oriented predominantly out of the interface.

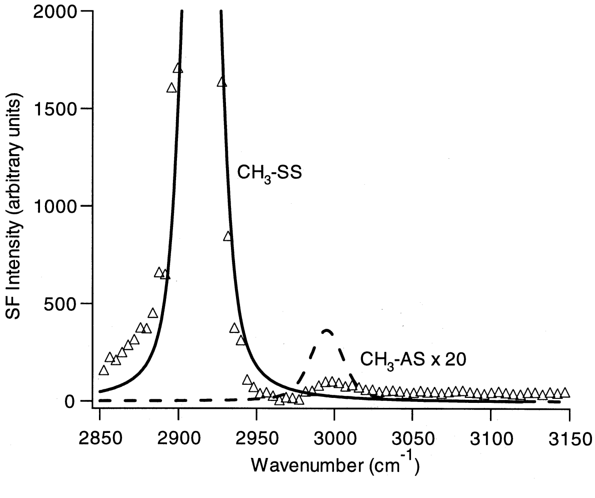

Fig. 2. Expanded spectrum of pure DMSO. The methyl SS peak (solid line) and AS peak (dotted line) contributions to the fit are shown. The AS peak has been multiplied by a factor of 20 for clarity.

Further studies with varied concentrations of DMSO and the other solutes have been conducted. For these spectra, water molecules at the surface also contribute. Therefore, a brief discussion of the SSP spectrum of neat water (Fig. 3) is warranted. The broad band from ~ 3000 to 3600 cm^{-1} is assigned to the broad distribution of OH hydrogen bonding stretching modes in which the oxygen is tetrahedrally coordinated [24–29]. The energy region from ~ 3000 to 3250 cm^{-1} is attributed to strong intermolecular hydrogen bonds of water molecules which give rise to a highly correlated hydrogen bonding network, assigned to OH symmetric stretches, ν_1. The higher energy broad band region (~ 3250–3600 cm^{-1}) is assigned to more weakly correlated hydrogen bonding stretching modes of molecular water that encompasses both ν_1 (OH symmetric stretch), and to a lesser extent, ν_3 (OH asymmetric stretch). The peak at 3702 cm^{-1} is assigned to the OH dangling bond, or free OH stretch, of 3 and 2 subsurface-coordinated molecules [26,30]. On either side of the dangling OH are the symmetric and asymmetric stretches of vapor water molecules, oriented with their hydrogens towards the water surface [2]. These two modes have a well-defined phase relationship to each other [4], similar to that of the methyl symmetric and asymmetric stretches. In addition, the SF signal from the oriented vapor and that from the dangling OH interfere, producing the lack of intensity at 3650 cm^{-1} and the shoulder at ~ 3760 cm^{-1}.

A spectrum of a 0.1 mole fraction (mf) solution of DMSO in water is shown in Fig. 4. The CH_3-SS is

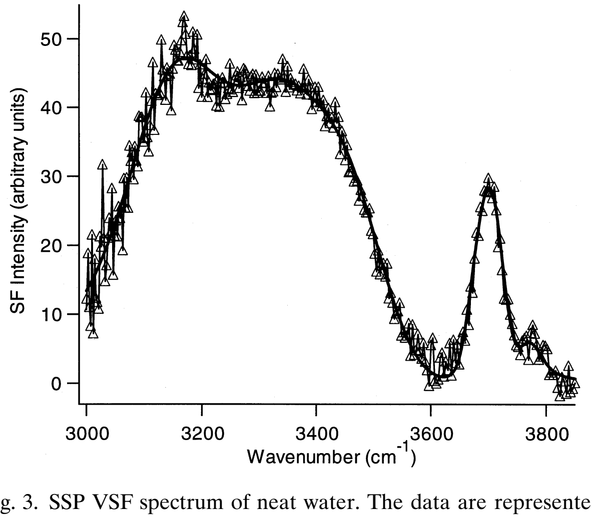

Fig. 3. SSP VSF spectrum of neat water. The data are represented by connected triangles, while the thick line is the fit to the data.

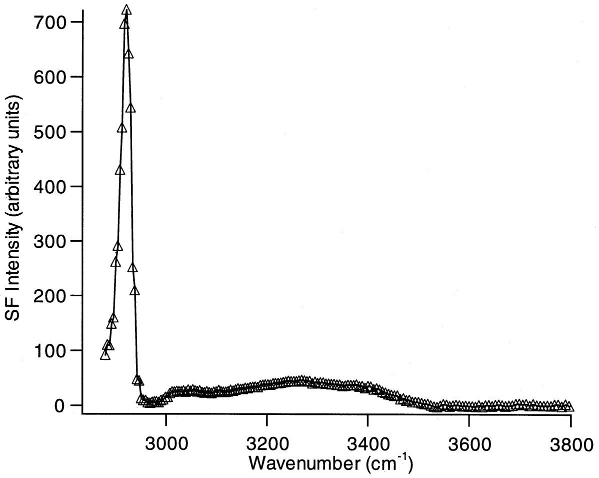

Fig. 4. VSF spectrum of an aqueous 0.1-mf DMSO solution. The solid line is a guide to the eye.

slightly shifted to higher energy relative to pure DMSO and has decreased in VSF intensity relative to pure DMSO. The asymmetry of the CH_3-SS observed for pure DMSO is still present. This is expected due to the inherent phase difference between the CH_3-SS and the CH_3-AS VSF responses. In addition, the region between 3000 and 3500 cm^{-1} has increased in intensity relative to pure DMSO. We attribute this broad band to the SS and to a lesser extent, the AS of surface water.

The shift to higher energy of the CH_3-SS has been attributed to a decreased interaction of the DMSO sulfur lone pair with the *trans*-CH of the methyl groups of DMSO [1]. This decreased interaction is indicative of the changing orientation of DMSO with surface concentration due to reduced aggregation [31] and crowding of the surface DMSO molecules. At lower concentrations the DMSO molecules aggregate to a lesser extent and it becomes more probable for the lone pair to interact in a perturbative manner with the surrounding surface water molecules than with the adjacent DMSO molecules. The magnitude of the decrease in VSF intensity of the CH_3-SS for the 0.1-mf DMSO solution (Fig. 4) compared to the pure DMSO CH_3-SS (Fig. 1) is not consistent with a simple decrease in the number of DMSO molecules at the surface. If this was the case, the surface number density taken from surface tension measurements and the square root of the VSF intensity should follow the same curvature with increasing concentration, which was not observed [1]. Both the frequency shift and the discrepancy between the SF intensity and the surface number density, indicate that as the surface concentration of DMSO increases, the DMSO molecules are aggregating and reorienting, such that the two methyl groups are becoming more perpendicular to the solution surface.

In the hydrogen bonding region of surface water (3000–3600 cm^{-1}), the increase in VSF intensity between the pure and 0.1 mf DMSO is consistent with an increase in the number of water molecules in the surface region. Interestingly, there is slightly more intensity in the 3300–3400 cm^{-1} region as compared to the 3190 cm^{-1} region. Comparing the relative intensity of these two regions with the pure water spectrum, a decrease in intensity from the cooperative intermolecular hydrogen bonding modes of the surface water appears to occur in the presence of DMSO. Bulk DMSO–water Raman studies also show a disordering influence introduced by adding DMSO to a water solution [32]. This disordering can be attributed to the strength of the hydrogen bonds that DMSO forms with water, they are stronger than those between water molecules [33], thereby effectively disrupting the long-range order of the hydrogen bonding network.

To further explore the adsorption and surface structure of small molecules of atmospheric relevance, VSFS studies of methane sulfonic acid were completed [3]. Fig. 5 shows a SSP VSF spectrum of a 0.1-mf MSA aqueous solution. The peak at 2940 cm^{-1} is assigned to the CH_3-SS of MSA and intensity around 3030 cm^{-1} is attributed to the CH_3-AS. The asymmetric peak frequency was determined by fitting the spectra with the appropriate phases to the peaks. Again the strong asymmetry of the CH_3-SS is assigned to the destructive interference between the two methyl stretching modes. The VSFS intensity centered around 3100 cm^{-1} is assigned to the cooperative intermolecular hydrogen bonding modes of surface water. There is an additional broad band of intensity centered at a lower frequency than is measured here, which is attributed to the proton transfer continuum consistent with MSA's strongly acidic nature. The proton contin-

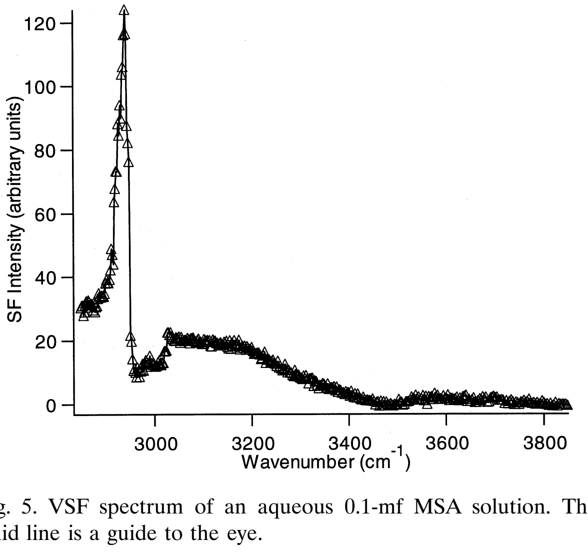

Fig. 5. VSF spectrum of an aqueous 0.1-mf MSA solution. The solid line is a guide to the eye.

uum for MSA has also been observed in infrared and Raman spectra of bulk MSA [34].

Comparing the VSF spectra from the 0.1-mf MSA solution and the 0.1-mf DMSO solution, there are several important differences. The relative intensity difference in the CH_3-SS peak between the DMSO and MSA spectra results from the two methyl groups of DMSO in addition to the increased polarizability of DMSO due to the sulfur lone pair. The region of destructive interference is also different between the MSA and DMSO spectra. The VSF intensity drop in Fig. 5 is square in shape in contrast to the dip observed for the DMSO spectra. The square shape of the intensity drop for the 0.1-mf MSA spectrum in Fig. 4 is primarily due to the underlying proton continuum and the increased separation in frequency of the CH_3-SS to the CH_3-AS, relative to the DMSO peak separation. As the concentration of MSA is increased from very low bulk values to pure MSA, the frequencies of the CH_3-SS and CH_3-AS maintain their positions. Additionally, the square root of the SF intensity tracks with the surface number density obtained from surface tension measurements [3]. These two pieces of information lead to the conclusion that unlike DMSO, the methyl group of surface MSA does not reorient as a function of surface concentration.

In addition to the differences in the CH stretching region, the surface water structure of aqueous MSA solutions undergoes significant changes as the concentration of MSA increases. As more MSA is present at the interface, the intensity of the free OH peak rapidly decreases, indicating that these surface species are being either bound or displaced from the interface. In addition there is a large decrease in the SF intensity due to the hydrogen bonded surface water molecules as MSA surface concentration increases. This decrease is most dramatic in the 3300–3600 cm^{-1} region, which corresponds to water molecules that are less strongly hydrogen bonded than those observed at lower frequencies. The net result is that the remaining surface water is more ordered than the water found at a neat water interface. This is in contrast to the aqueous DMSO surface (Fig. 4), in which the remaining surface water appears to be less ordered than a neat interface. This difference in the surface structure can be attributed to the different ways MSA and DMSO interact with water. As previously mentioned, DMSO forms very strong hydrogen bonds with the surrounding water molecules, thereby effectively disrupting the hydrogen bonding network formed between water molecules. MSA on the other hand, is a strong acid ($pK_a = -1.9$) [35], and at low solution concentrations is completely ionized. Two possible factors responsible for this apparent enhancement of surface hydrogen bonding are the presence of ions in the surface region and the additional contribution of water molecules in the tight double layer formed by the dissociation of the MSA [36].

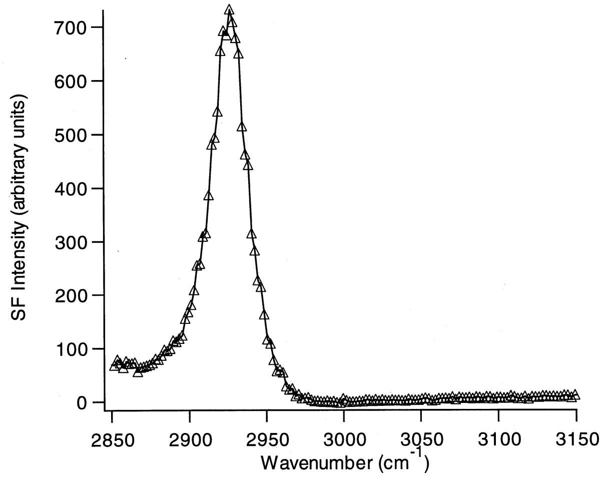

Fig. 6. VSF spectrum of an aqueous 0.1-mf acetone solution (solution temperature of ~ 15°C). The solid line is a guide to the eye.

Acetone, in addition to having a significant population in the atmosphere, has a similar structure to DMSO, with the more electronegative sulfur being replaced by a carbon atom. The spectrum of a 0.1-mf acetone solution shown in Fig. 6, taken with a solution temperature of 15°C, exhibits a large peak at 2926 cm^{-1}, assigned to the CH_3-SS mode, (bulk Raman and IR studies assign this peak to 2922 and 2924 cm^{-1}, respectively) [37]. The lack of signal in the hydrogen bonding region of the spectrum is consistent with the higher surface activity of acetone, indicating that the surface population is dominated by acetone. The asymmetry of the CH_3-SS peak is again attributed to the destructive interference between the symmetric and asymmetric stretch modes. The destructive interference between the methyl symmetric and asymmetric stretches of acetone is less distinct than that observed for either DMSO or MSA, primarily due to the narrow separation between the two peaks (~ 43 cm^{-1} for acetone, ~ 84 cm^{-1} for DMSO and 89 cm^{-1} for MSA). Despite the difference in appearance of the destructive interference in the DMSO, MSA and acetone spectra, all three sets of spectra can be fit in the same manner, with the interpretation that the surface methyl groups are preferentially oriented away from the bulk liquid.

4. Conclusions

In this paper we demonstrate the utility of using VSFS to study three atmospherically relevant molecules adsorbed at the air/water interface. These studies have shown that DMSO, MSA, and acetone all preferentially partition to aqueous surfaces, and the molecular structure at the interface is controlled by the nature of the interactions between the surface molecules. All three molecules tend to orient such that their methyl groups are pointing away from the bulk, but the actual structure of both the adsorbed molecules and the remaining surface water is strongly controlled by the type of molecular interactions. The resulting surface composition and structure of aerosols in the troposphere plays a large role in determining which adsorption processes occur, as well as controlling the rates of these processes. The demonstrated use of VSFS to probe interfaces containing small quantities of adsorbed molecules opens up many opportunities for future studies of the molecular structure and surface reactivities of atmospherically important molecules at water surfaces.

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