SO2:H2O Surface Complex Found at the Vapor/Water Interface

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In recent years, it has become clear that the air/water interface plays a much larger role in gas adsorption and reaction kinetics of many atmospheric processes than scientists had previously anticipated. Recently, surface complexes have been invoked to explain the initial step in a number of surface reaction mechanisms,[1−4] including the reaction of gas phase SO_2 with water.[5] Understanding SO_2 interactions at aqueous surfaces is essential due to the central role of sulfur species in many atmospheric aerosols.

There is an ongoing debate about the existence and composition of SO_2 complexes in the interfacial region.[5−9] SO_2:water surface complexes were first proposed by Jayne et al.[5] Since the SO_2−water reaction is facile, Jayne et al.[5] assigned the predominate interfacial species as HSO_3^- −H^+ to account for the greater SO_2 uptake than that predicted by kinetic models of bulk solution at low pH.[5] However, more recent measurements suggest the uptake coefficients can be determined from the bulk reaction rate constant.[10] Surface second harmonic generation studies of sodium bisulfite solutions suggested evidence for a surface complex.[8] Subsequent MD simulations[9] suggest that a 1:1 SO_2:H_2O surface complex is not stable enough to be this species. Recent studies using ATR−FTIR did not show evidence of a hydrate.[6]

The present studies report results of vibrational sum-frequency spectroscopy (VSFS) experiments that directly address the issue of the existence of SO_2 species in the interfacial region. VSFS is a second-order nonlinear optical spectroscopy that probes the vibrational resonances of molecules in anisotropic environments.[11] It is a unique way of determining surface structure, chemical identity, and molecular orientation in the interfacial region, distinguishing between SO_2 adsorbate products and surface active organic contaminates commonly found in aerosols. In this study, changes to the interfacial water structure in the presence of SO_2 gas are examined. The results indicate that both an SO_2 surface complex and dissolved SO_2 reaction products are present in the interfacial region upon exposure of the vapor/water interface to SO_2 gas.

A considerable effort[12−17] has been devoted to elucidating the structure, depth, and orientation of water molecules in the interfacial region. For example, it is generally accepted that the depth of the interfacial region is small ($\sim$6−9 Å),[14,17] the water dipole is oriented close to the interfacial plane,[15,17,18] and water molecules with few hydrogen bonding interactions are present in the topmost surface layer.

A sum-frequency spectrum of the neat vapor/water interface is shown in gray in Figure 1a for a selected polarization that probes modes with transition dipoles perpendicular to the surface. The assignment of the interfacial OH stretching modes has been described in previous publications of detailed interfacial isotopic dilution experiments,[17,19,20] and the current data are fit with similar parameters. The topmost surface water molecules with the weakest hydrogen bonding interactions occur in the 3500−3700 cm^{-1} region of the spectrum. The sharp feature at 3700 cm^{-1} corresponds to the free OH bond that points into the air with its companion "donor"
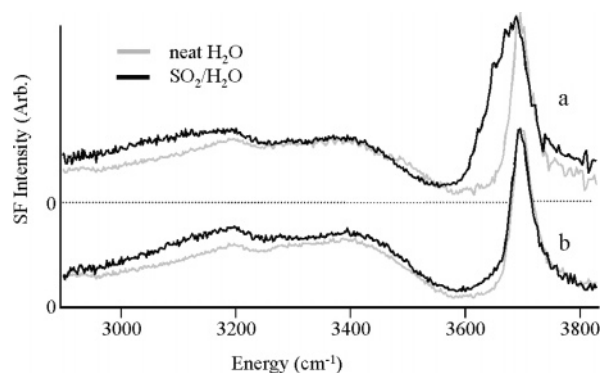

Figure 1. Sum-frequency spectra of SO_2 gas at the vapor/water interface in the OH stretching region with *ssp*-polarization. (a) SO_2 gas is flowing (black); neat vapor/water spectrum (gray). (b) Immediately after SO_2 gas is turned off (black); neat vapor/water spectrum (gray).

OH bond ($\sim$3460 cm^{-1}), which the hydrogen can act as a proton donor and/or the oxygen as a weak electron pair donor with other surface water molecules.[21−23] Other weakly interacting water molecules in this topmost layer are predominately oriented with their dipoles nearly parallel to the interfacial plane[17] (and appear in the *sps*-polarization spectra near 3600 cm^{-1}). Intensity below 3400 cm^{-1} corresponds to somewhat deeper interfacial water molecules that strongly bond with tetrahedral coordination to their neighbors. The orientation and bonding of these deeper interfacial water molecules are very sensitive to surface dipole and electric field effects that extend the surface region to allow more tetrahedrally coordinated water molecules to contribute to the VSFS response.

The change in the VSF spectrum found on exposure of SO_2 to the water surface is also displayed in Figure 1a. The vapor/water interface was under an atmosphere of SO_2 with the gas continually flowing maintaining $\sim$1 atm pressure. Due to the nature of the spectral interferences, detailed interpretation of the spectra requires data fitting routines that have been previously established.[24] We summarize the results here with more quantitative fitting information in a later publication. The most striking change is a shoulder on the free OH peak, which appears here as a broadening of that peak. Fits to the spectra indicate that in the presence of SO_2 an additional OH vibrational resonance occurs at $\sim$3675 cm^{-1}. We attribute this to a weak bonding interaction between SO_2 gas and the water molecules in the top surface layer, an SO_2:H_2O surface complex. The lower peak frequency of the surface complex suggests a bonding interaction, and the breadth of the peak is indicative of a range of bonding environments between SO_2 and surface water. Interestingly, we easily observe the SO_2:H_2O complex even in the presence of surface organic contaminants.

Figure 2 shows a cartoon of the two possibilities for bonding in a 1:1 SO_2:H_2O surface complex, the oxygen of SO_2 bonding to the hydrogen atom of water (A) or the sulfur atom of SO_2 bonding to the oxygen atom of water (B). In the first case, water acts as a π
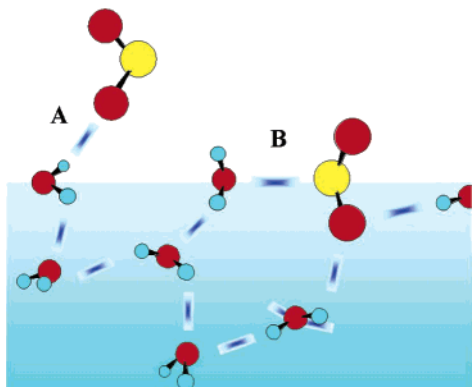
Figure 2. A cartoon of the SO₂/air/water interface. Possible SO₂:water complexes are depicted: the oxygen of SO₂ bonding to the hydrogen atom of water (A) and the sulfur atom of SO₂ bonding to the oxygen atom of water (B).

electron acceptor (hydrogen bonding interaction), and in the second case, water acts as a lone pair donor toward the sulfur of SO_2, effectively making the hydrogen atom of the water molecule more acidic, which red shifts the unbound OH mode. Evidence for both of these interactions, water acting as a lone pair donor and a π electron acceptor, has been seen in low-temperature matrix and FTIR film studies.[25,26] Microwave spectra of the SO_2:H_2O complex show bonding between the sulfur atom of SO_2 and the oxygen atom of water.[27] On the basis of the out of plane orientation of the complex mode, our sum-frequency results suggest the interaction is type A. Although we assign the mode a 1:1 SO_2:H_2O surface complex, contributions from a 1:2 complex or other hydrates are possible. One reason we may not observe a straddling SO_2 molecule (type B) is that it may quickly react with water.

Intensity changes are also observed in the tetrahedrally bonded region. These increases are attributed to the presence of reaction products of SO_2 and water, H^+ and HSO_3^-, in the interfacial layer that lead to spectral increases in the tetrahedrally coordinated modes. Protons elicit strong electrostatic interactions, and HSO_3^- has strong ion−dipole interactions with water that can contribute to the interfacial field and an increased tetrahedral bonding network. This analysis is supported by a series of studies of the effect of added $NaHSO_3$, Na_2SO_3, $NaHSO_4$, and Na_2SO_4 salts that give insight into contributions from the pH, ionic strength, and the nonresonant response.[28] These anions are large, polarizable, and capable of hydrogen bonding. There are several possible contributions to the increase in intensity for the tetrahedrally coordinated OH stretching region: strong ion−dipole interactions that can increase the transition strength of the vibrations of interfacial water molecules, greater water dipole alignment along the surface normal, and increased interfacial depth that the VSF probes due to an increased electric field.

The SO_2 complex that we observe is indeed short-lived. As shown in Figure 1b, once the SO_2 gas flow over the surface is stopped, the free OH region of the spectrum returns to being a single peak. However, the spectral changes attributed to ionic species in solution remain. More detailed studies of this complex and its stability are in progress.

These studies clearly demonstrate the presence of a weak SO_2:H_2O complex at the water surface prior to reaction and dissolution into the aqueous boundary layer. These results are important in elucidating the structure and composition of aerosol particles, of which sulfur species play a key role. Since aqueous aerosol particles have a very large surface area relative to their bulk volume, observing this complex at the vapor/water interface has important implications for understanding the formation and composition of sulfur-containing aerosols.

References

(1) Knipping, E. M.; Lakin, M. J.; Foster, K. L.; Jungwirth, P.; Tobias, D. J.; Gerber, R. B.; Dabdub, D.; Finlayson-Pitts, B. J. *Science* **2000**, *288*, 301−304.
(2) Hu, J. H.; Shi, Q.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1995**, *99*, 8768−8776.
(3) Hanson, D. R.; Ravishankara, A. R. *J. Phys. Chem.* **1994**, *98*, 5728−5735.
(4) George, C.; Behnke, W.; Scheer, V.; Zetzsch, C.; Magi, L.; Ponche, J. L.; Mirabel, P. *Geophys. Res. Lett.* **1995**, *22*, 1505−1508.
(5) Jayne, J. T.; Davidovits, P. *J. Phys. Chem.* **1990**, *94*, 6041−6048.
(6) Yang, H.; Wright, N. J.; Gagnon, A. M.; Gerber, R. B.; Finlayson-Pitts, B. J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1832−1838.
(7) Boniface, J.; Shi, Q.; Li, Y. Q.; Cheung, J. L.; Rattigan, O. V.; Davidovits, P.; Worsnop, D. R.; Jayne, J. T.; Kolb, C. E. *J. Phys. Chem. A* **2000**, *104*, 7502−7510.
(8) Donaldson, D. J.; Guest, J. A.; Goh, M. C. *J. Phys. Chem.* **1995**, *99*, 9313−9315.
(9) Bishenden, E.; Donaldson, D. J. *J. Phys. Chem. A* **1998**, *102*, 4638−4642.
(10) Shimono, A.; Koda, S. *J. Phys. Chem.* **1996**, *100*, 10269−10276.
(11) Bain, C. D. *Surf. Sci. Ser.* **1999**, *83*, 335−373.
(12) Wei, X.; Shen, Y. R. *Phys. Rev. Lett.* **2001**, *86*, 4799−4802.
(13) Wilson, K. R.; Cavalleri, M.; Rude, B. S.; Schaller, R. D.; Nilsson, A.; Pettersson, L. G. M.; Goldman, N.; Catalano, T.; Bozek, J. D.; Saykally, R. J. *J. Phys.: Condens. Matter* **2002**, *14*, L221−L226.
(14) Dang, L. X.; Chang, T.-M. *J. Chem. Phys.* **1997**, *106*, 8149−8159.
(15) Morita, A.; Hynes, J. T. *Chem. Phys.* **2000**, *258*, 371−390.
(16) Morita, A.; Hynes, J. T. *J. Phys. Chem. B* **2002**, *106*, 673−685.
(17) Raymond, E. A.; Tarbuck, T. L.; Brown, M. G.; Richmond, G. L. *J. Phys. Chem. B* **2003**, *107*, 546−556.
(18) Vassilev, P.; Hartnig, C.; Koper, M. T. M.; Frechard, F.; van Santen, R. A. *J. Chem. Phys.* **2001**, *115*, 9815−9820.
(19) Raymond, E. A.; Richmond, G. L. *J. Phys. Chem. B* **2004**, *108*, 5051−5059.
(20) Raymond, E. A.; Tarbuck, T. L.; Richmond, G. L. *J. Phys. Chem. B* **2002**, *106*, 2817−2820.
(21) Buch, V. *J. Phys. Chem. B* **2005**, *109*, 17771−17774.
(22) Walker, D.; Richmond, G. L. Manuscript in preparation.
(23) Perry, A.; Neipert, C.; Kasprzyk, C. R.; Green, T.; Space, B.; Moore, P. B. *J. Chem. Phys.* **2005**, *123*, 144705.
(24) Bain, C. D.; Davies, P. B.; Ong, T. H.; Ward, R. N.; Brown, M. A. *Langmuir* **1991**, *7*, 1563−1566.
(25) Schriver, A.; Schriver, L.; Perchard, J. P. *J. Mol. Spectrosc.* **1988**, *127*, 125−142.
(26) Schriver-Mazzuoli, L.; Chaabouni, H.; Schriver, A. *J. Mol. Struct.* **2003**, *644*, 151−164.
(27) Matsumura, K.; Lovas, F. J.; Suenram, R. D. *J. Chem. Phys.* **1989**, *91*, 5887−5894.
(28) Tarbuck, T. L.; Richmond, G. L. Submitted to *J. Am. Chem. Soc.*

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