

SO₂ Adsorption onto Aqueous Aerosol Surfaces

Climate change has been impacting the earth since the onset of the Industrial Revolution and the advent of modern industrial processes. Nearly 12,000 Tg of biogenic aerosols are emitted into the atmosphere every year, accounting for approximately 98% of all aerosol emissions.¹ While the majority of aerosols arise from natural sources such as the ocean, emission of hazardous chemicals largely arises from anthropogenic sources including transportation, factories, and cleaning solvents. The surface of aqueous aerosols provides a region for heterogeneous chemical reactions to occur between these hazardous chemicals and other atmospheric species that would be otherwise unlikely.² The adsorption of air pollutants onto the surface of aerosols has become a major topic of research in recent years due to the deteriorating environment. The full effect of aerosols on the environment is not fully understood, and researchers are attempting to understand how chemistry at the air-water interface is able to differ from chemistry in bulk phases.

Aerosols can range in size from a few nanometers to tens of microns, and have high surface areas per total volume.² Previous computational studies have found the hydrogen-bonding network at the air-water interface to be much looser than the network in the bulk phase, and the interface region is generally accepted to be between 6-9 Å deep.^{3,4} This region of looser hydrogen bonding is well suited for the adsorption of atmospheric species, such as SO₂ and CO₂. Experimental studies of the interfacial region are difficult due to the need for a surface-specific technique.⁵ Vibrational sum frequency spectroscopy (VSFS) first emerged as a method to study the surface of the air-water interface in 1993.⁶ Sum-frequency generation, a second-order non-linear process, is dipole forbidden in isotropic media but can occur at interfaces where inversion symmetry is broken. Briefly, an 800 nm light source is overlapped spatially and temporally at the surface being studied with a tunable IR source, and the sum frequency signal is monitored as the tunable source is scanned across its range (Figure 1).⁷

VSFS has been used to study the adsorption of a variety of air pollutants onto aerosol surfaces, including halide anions, SO₂, volatile organic compounds, and other relevant atmospheric molecules. In order to imitate atmospheric conditions, interfacial studies must be performed at temperatures ranging from 0°C to 23°C. Richmond and co-workers probed the surface of a water droplet at six different temperatures and examined the resulting vibrational spectra with and without the presence of SO₂. A broadened peak in the free-OH stretching region (3700 cm⁻¹) was attributed to the presence of a new peak at 3650 cm⁻¹, representing the free OH complexed to SO₂. A broad peak at 3150 cm⁻¹ that appears only in the presence of SO₂ is attributed to enhanced OH coordination. These

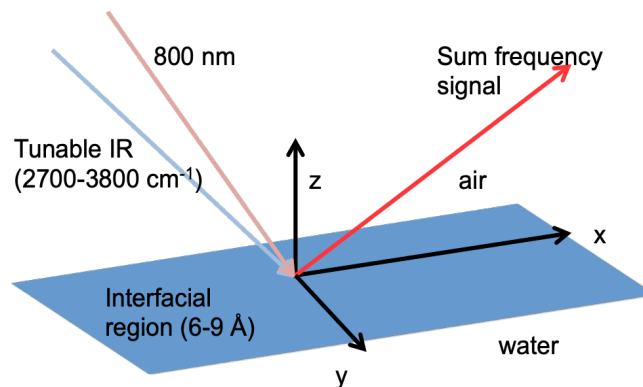


Figure 1. Schematic of VSFS experiment: An 800 nm pulse is mixed with a tunable IR pulse in space and time at 54° and 67° normal to the interfacial surface, respectively.

features were enhanced as temperature was lowered (**Figure 2**), leading to the conclusion that SO₂ adsorption to the water surface increases with decreasing temperature.⁸

It is only within the past few years that molecular dynamics simulations have begun to examine the microscopic behavior of SO₂ adsorbed onto the surface of a water droplet. In 2013, Richmond and co-workers performed *ab initio* Molecular Dynamics simulations to characterize the hydration environment of SO₂ at the surface of a water droplet. Simulations were performed at 300 K and at 210 K to mimic conditions of the upper troposphere. The simulations found that the most popular bonding interactions between SO₂ molecules and surface water were “S,” “SO,” and “SOO,” which involve a single bond through the sulfur, and one and two bonds with the sulfur oxygens, respectively. The room temperature simulation found a 4.6% reduction in “S” interactions and an 8.6% reduction in “SOO” interactions, as compared to the 210 K simulation.⁹ This is in agreement with the findings from VSFS experiments at the SO₂:H₂O interface performed at a variety of temperatures, indicating that SO₂ is more effectively able to interact with surface water molecules at colder temperatures, such as those of the upper troposphere.

Richmond and co-workers were able to form a picture of the typical bonding interactions of an SO₂ molecule at the interface. In the 300 K simulation, the SO₂ molecules at the surface were twice as likely to be unbound. The SO₂ is then likely to form one bonding interaction through the sulfur atom, and subsequently will form either one or two bonding interactions through one of its oxygen atoms. This information about how the SO₂ binds to surface waters will help future researchers to understand the exact mechanism of how SO₂ is able to undergo heterogeneous reactions to form secondary pollutants.

In 2017 Francisco and co-workers investigated the adsorption of SO₂ onto the surface of various sizes of nanodroplets using Born-Oppenheimer Molecular Dynamics simulations. Because of the wide spread of aerosol particle sizes in the atmosphere, it is important to examine the differences of gas adsorption onto the surface of different sized aqueous aerosol particles. The simulation was run with water droplet sizes of 24, 48, 96, and 191 water molecules, and the results showed that decreasing droplet size increases the probability that SO₂ molecules will not be bound to the surface water molecules.¹⁰ Interestingly, the results showed that the most probable interaction between SO₂ and water molecules on the surface of a nanodroplet is through the oxygen atom of the SO₂, which is the same finding in the MD simulations performed by Richmond and co-

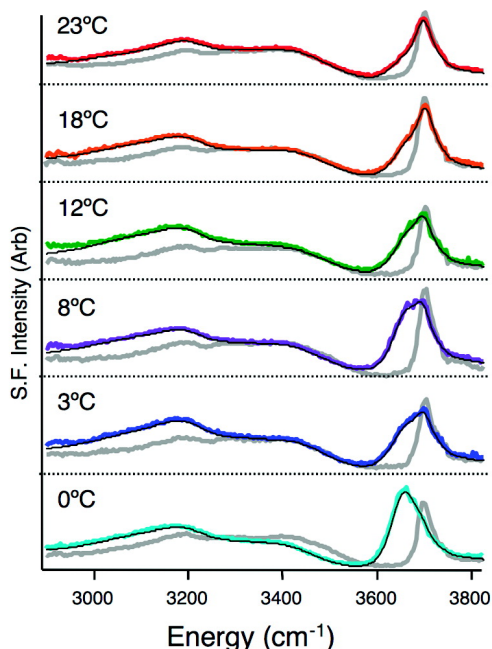


Figure 2: Experimental VSFS of the neat H₂O:air interface (gray traces) and the H₂O:SO₂ interface (colored traces) at different temperatures.

workers that were performed at 300 K. The report from Richmond examined adsorption as a function of temperature only, and the report from Francisco examined adsorption as a function of droplet size only. In order to understand the full effects of droplet size and temperature on SO₂ adsorption, further simulations must be performed.

In addition, these simulations only studied the adsorption behavior of SO₂ onto a droplet of pure water. While many experiments using VSFS have been performed to study SO₂ adsorption onto the surface of water with common organic atmospheric pollutants, molecular dynamics simulations must be performed to understand exactly how chemical reactions in the interfacial region lead to secondary atmospheric pollutants.

References

- [1] Viana, M.; Pey, J.; Querol, X.; Alastuey, A.; de Leeuw, F.; Lükewille, A. Natural Sources of Atmospheric Aerosols Influencing Air Quality across Europe. *Sci. Total Environ.* **2014**, *472*, 825–833.
- [2] Zhong, J.; Kumar, M.; Anglada, J. M.; Martins-Costa, M. T. C.; Ruiz-Lopez, M. F.; Zeng, X. C.; Francisco, J. S. Atmospheric Spectroscopy and Photochemistry at Environmental Water Interfaces. *Annu. Rev. Phys. Chem.* **2019**, *70* (1), 45–69.
- [3] Tainter, C. J.; Ni, Y.; Shi, L.; Skinner, J. L. Hydrogen Bonding and Oh-Stretch Spectroscopy in Water: Hexamer (Cage), Liquid Surface, Liquid, and Ice. *J. Phys. Chem. Lett.* **2013**, *4* (1), 12–17.
- [4] Pieniazek, P. A.; Tainter, C. J.; Skinner, J. L. Interpretation of the Water Surface Vibrational Sum-Frequency Spectrum. *J. Chem. Phys.* **2011**, *135* (4).
- [5] Johnson, C. M.; Baldelli, S. Vibrational Sum Frequency Spectroscopy Studies of the Influence of Solutes and Phospholipids at Vapor/Water Interfaces Relevant to Biological and Environmental Systems. *Chem. Rev.* **2014**, *114* (17), 8416–8446.
- [6] Du, Q.; Superfine, R.; Freysz, E.; Shen, Y. R. Vibrational Spectroscopy of Water at the Vapor/Water Interface. *Phys. Rev. Lett.* **1993**, *70* (15), 2313–2316.
- [7] Gragson, D. E.; Richmond, G. L. Investigations of the Structure and Hydrogen Bonding of Water Molecules at Liquid Surfaces by Vibrational Sum Frequency Spectroscopy. *J. Phys. Chem. B* **1998**, *102* (20).
- [8] Ota, S. T.; Richmond, G. L. Chilling out: A Cool Aqueous Environment Promotes the Formation of Gas-Surface Complexes. *J. Am. Chem. Soc.* **2011**, *133* (19), 7497–7508.*
- [9] Shamay, E. S.; Valley, N. A.; Moore, F. G.; Richmond, G. L. Staying Hydrated: The Molecular Journey of Gaseous Sulfur Dioxide to a Water Surface. *Phys. Chem. Chem. Phys.* **2013**, *15* (18), 6893–6902.*
- [10] Zhong, J.; Zhu, C.; Li, L.; Richmond, G. L.; Francisco, J. S.; Zeng, X. C. Interaction of SO₂ with the Surface of a Water Nanodroplet. *J. Am. Chem. Soc.* **2017**, *139* (47), 17168–17174.*