In-Situ Analysis of the Bulk and Surface Chemical Compositions of Organic Aerosol Particles

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Abstract

Understanding of the chemical and physical properties of particles is an important scientific, engineering, and medical issue that is crucial to air quality, human health, and environmental chemistry. Of special interest are aerosol particles floating in the air for both indoor virus transmission and outdoor atmospheric chemistry. The growth of bio- and organic-aerosol particles in the air is intimately correlated with chemical structures and their reactions in the gas phase at aerosol particle surfaces and in-particle phases. However, direct measurements of chemical structures at aerosol particle surfaces in the air are lacking. Here we demonstrate in situ surface-specific vibrational sum frequency scattering (VSFS) to directly identify chemical structures of molecules at aerosol particle surfaces. Furthermore, our setup allows us to simultaneously probe hyper-Raman scattering (HRS) spectra in the particle phase.

Introduction

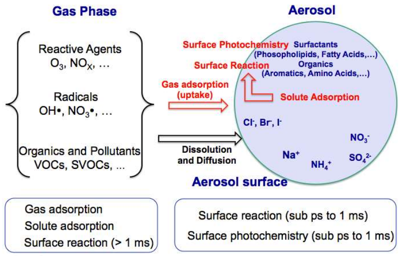

Figure 1. Kinetics & Reactions of Molecules at Aerosol Surfaces

Secondary organic aerosol formation is one of the greatest sources of uncertainty in estimations of aerosol climate forcing. The pathways for SOA formation can be simply pictured as gas uptake, diffusion, and reactions in the gas-phase atmospheric chemistry.

There is increasing evidence that the interface between the gas and aerosol particles does not act as a door-keeper, instead, represent a unique area for physical characters and chemical reactions. Understanding and quantifying the SOA requires knowledge of the chemistry and physics occurring at the interface between the reactive atmospheric gas and condensed phases.

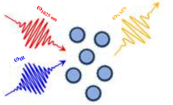

Figure 2. Schematic of VSFG from Particle Surfaces

Vibrational sum frequency scattering is a surface-sensitive technique. This method is based on the principle that a second-order nonlinear optical process is forbidden in a medium with inversion symmetry, but such symmetry will necessarily be broken at an interface. The electric field of SFG is proportional to the coverage of molecules at the aerosol surface.

$$E_{2\omega} \propto N_s$$

Experiments

Experimental Setup for Vibrational Sum Frequency Scattering (VSFS) and Hyper-Raman Scattering (HRS) Measurements

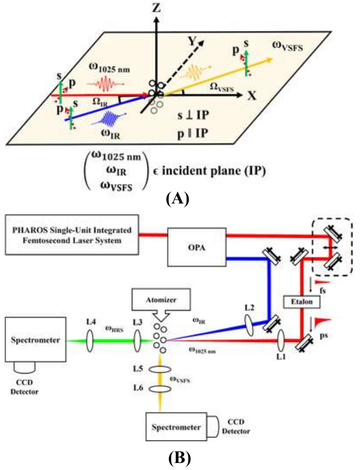

Figure 3. A) A schematic diagram of the beam management in VSFS experiments. A picosecond 1025 nm and a broadband IR light were non-collinearly incident on samples. B) Schematic diagram of both the VSFS and HRS experiments. A spectrally narrow picosecond 1025 nm from an etalon was combined with a broadband OPA-generated IR femtosecond pulse at the aerosol samples to yield sum-frequency and hyper-Raman signals.

Results and Conclusions

Comparison of VSFS and HRS Spectra for Aerosol Particles

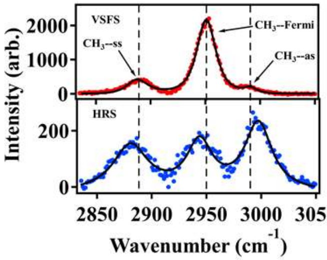

Figure 4. HHH-polarized configuration spectra for VSFS (upper) and HRS (lower) for aerosol particles from a 0.5 M NaCl seed solution with 4.0 M propionic acid.

Comparison of VSFS and HRS Isotherms for Aerosol Particles

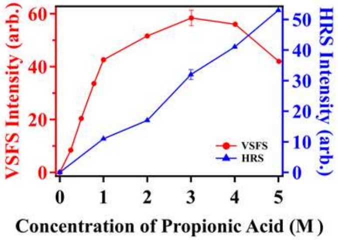

Figure 5. VSFS (red solid circle, left axis) and HRS (blue solid triangle, right axis) intensities at 2991.8 cm^{-1} (CH_3-as) as a function of propionic acid concentrations added. Error bars represent 5% deviation.

Polarization-dependent VSFS Spectra of Organic Species at Aerosol Particle Surfaces

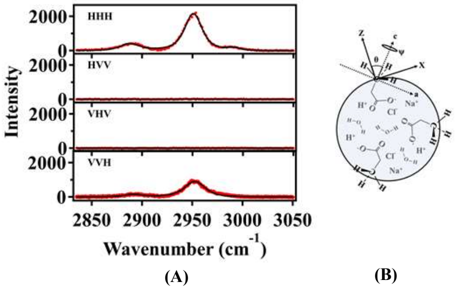

Figure 6. A) Polarized VSFS spectra for aerosol particles from 4 M propionic acid in a 0.5 M NaCl seed solution with HHH, HHV, HVH, and HVV. B) Schematic of orientational configuration of the $-CH_3$ group of propanoic acids at the aerosol surface.

Comparison of Aerosol Curved Surface and Air/Water Planar Interface

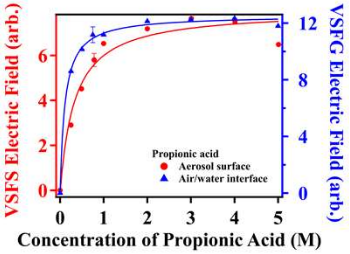

Figure 7. VSFS electric fields of CH_3-as for aerosol curved surfaces (red solid circle, right axis) and VSFG electric fields of CH_3-as for the air/water planar interface (blue solid triangle, right axis) as a function of propionic acid concentration in a 0.5 M NaCl seed solution. Error bars represent 5% deviation.

VSFS Isotherms of Different Organic Species at Aerosol Particle Surface

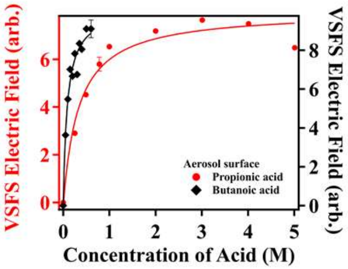

Figure 8. VSFS electric fields of $-CH_3$-as as a function of butanoic acid concentration in 0.5 M NaCl seed solution (black sold diamond, right axis), in comparison with those for propionic acid (red solid circle, left axis). Error bars represent 5% deviation.

Summary

We have presented in situ analysis of chemical structures of organic species at aerosol surfaces by developing and implementing vibrational sum frequency scattering spectroscopy. This unique setup also offered simultaneous chemical structure analysis of species by hyper-Raman scattering from the in-particle phase. Surface adsorption free energy of propionic acid at aerosol surfaces is lower than that at the air/water interface. These results imply that previous modeling of heterogeneous atmospheric chemistry by using data from the planar surface must be re-evaluated. The in situ VSFS method offers a direct approach for understanding the role of aerosol particle surfaces in real time. The development of the in situ simultaneous VSFS and HRS technique could also enlighten mechanistic studies of chemical reactions at aerosol surfaces and in-particle phases at the same time. Thus, we will be able to differentiate surface from bulk contributions to the production of large organic compounds in aerosol particles.

Reference

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