In-Situ Spectroscopic Probing of Polarity and Molecular Configuration at Aerosol Particle Surfaces

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Abstract

The growth of aerosol particles in the atmosphere is related to chemical reactions in gas phase, particle phase, and at aerosol particle surfaces. While researches in the gas and particle phases of aerosols are well documented, physical properties and chemical reactivities at aerosol particle surfaces have not been studied extensively but have long been recognized. In particular, in situ measurements of aerosol particle surfaces are just emerging. The main reason is a lack of suitable surface-specific analytical techniques for direct measurements of aerosol particles under ambient conditions. Here we develop in situ surface-specific electronic sum frequency scattering (ESFS) to directly identify spectroscopic behaviors of molecules at aerosol particle surfaces.

Introduction

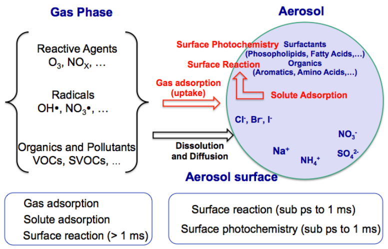


Figure 1. Kinetics & Reactions of Molecules at Aerosol Surfaces

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.

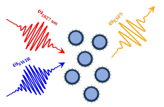
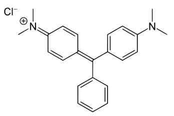


Figure 2. Schematic of ESFG from Particle Surfaces

Electronic 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.

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



Malachite Green

Experiments

Experimental Set-up for Electronic Sum Frequency Scattering (ESFS) Measurements

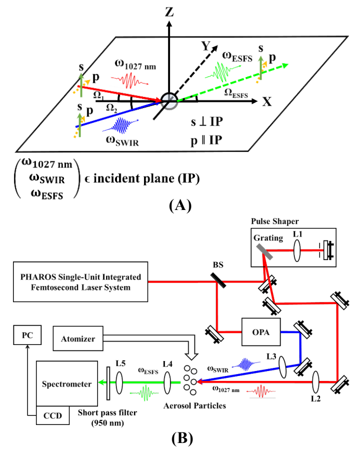


Figure 3. A) A schematic diagram of the beam management in ESFS experiments. A picosecond 1027 nm and a SWIR light were non-collinearly incident on samples. B) A schematic setup for ESFS measurements for aerosol particle surfaces. The picosecond 1027 nm was generated from a home-built pulse shaper. It was composed of four main units, including Laser sources, beam managements, generation of particles, and detection of ESFS signal.

Coherent ESFS and Incoherent Hyper Rayleigh Scattering (HRS)

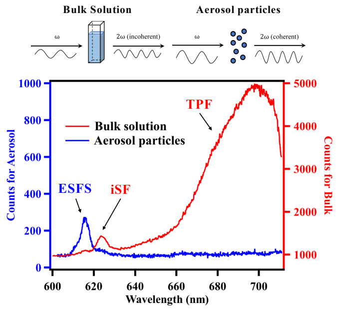


Figure 5. Emission spectra of bulk solution (red) and aerosol particles (blue) from a same solution of 1.0 M NaCl with 200 μM MG, by mixing a picosecond 1027 nm laser and a femtosecond 1550 nm SWIR light temporally and spatially. ESFS: coherent electronic sum frequency scattering; iSF: incoherent sum frequency; TPF: two-photon fluorescence.

Number Density and Surface Area Distributions of Aerosol Particles

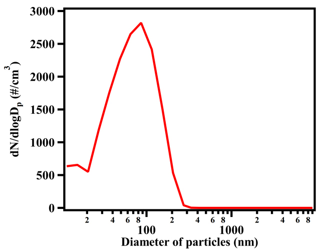


Figure 4. Aerosol number distribution generated from a seed solution of 1.0 M NaCl, plotted against the logarithm of the diameter of the particles. The number distribution was taken after 100 times dilution of the original aerosol particles from the atomizer. Dp represents the diameter of a particle.

Results and Conclusions

Polarization-dependent ESFS Spectra of MG at Gas-aerosol Particle Interfaces

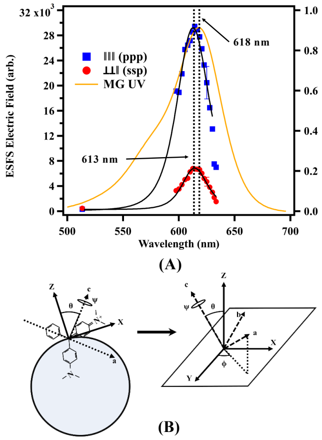


Figure 6. A) Polarization-dependent ESFS spectra of MG from aerosol particles from 1.0 M NaCl solution mixed with 14 mM MG as compared with UV-Vis absorption of MG in bulk solution (solid line). The solid lines (black) are fitted results. B) Orientational configuration of MG at an aerosol particle surface. θ is defined as a polar angle of the axis c, which is perpendicular to the molecular symmetric axis a of MG.

ESFS Isotherms of Aerosol Particles

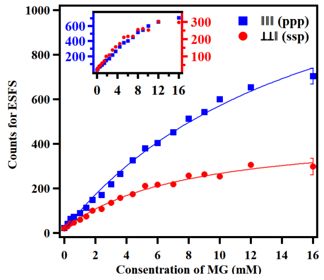


Figure 7. ESFS isotherms of aerosol particles generated from 1.0 M NaCl solution mixed with desired concentrations of MG. A picosecond 1027 nm laser was mixed with 1550 nm femtosecond SWIR for SSP (red solid circle) and PPP (blue solid square) polarizations, respectively. The inset is the comparison of the normalized isotherms for the two polarization combinations.

Summary

1. We have for the first time demonstrated in situ spectroscopic identification of organic species at aerosol particle surfaces with the development of electronic sum frequency scattering technique.
2. The electronic responses of MG were found to be blue-shifted with respect to that in its bulk solution. The blue shift in the ESFS was due to the more hydrophobic nature at the aerosol particle surfaces as compared with that in its bulk.
3. Surface population of MG has been found to exhibit distinct behaviors at the surfaces from the planar air/water interface.
4. Our experimental findings from the novel technique stress the importance of physical properties and chemical activities on aerosol particle surfaces.

Reference

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