

Simultaneous Characterization of n-Alcohols (C=1-4) at and Below Aerosol Surfaces

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Abstract

Atmospheric aerosol particles are abundant and ubiquitous in both indoor and outdoor environments. While it is widely accepted that the evolution of aerosol particles in the atmosphere is closely connected to interface-specific phenomena, most relevant methods are invasive and destructive. Here we present vibrational sum frequency scattering (VSFS) spectroscopy for interfacial vibrational characterization of n-alcohols (C=1-4) at the gas/aerosol particle interface. Additionally, we demonstrate interfacial differences between aerosol particles and their planar analogue. VSFS offers interfacial characterization at the gas/aerosol particle surface and questions the relationship between gas/aerosol and planar air/liquid interfaces.

Introduction

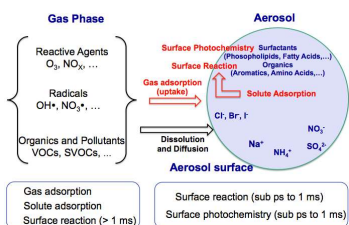


Figure 1. Kinetics & Reactions of Molecules at Aerosol Surfaces

The formation and growth of secondary organic aerosols is of great concern to chemists and environmental scientists alike. The culprit causes are gas-phase reactions, heterogeneous reactions at the gas/aerosol particle interface, and bulk-phase reactions with adsorbates.

The unique chemical and physical properties of the gas/aerosol particle interface result in enhanced reaction and uptake rates, as well as altered light scattering and absorption properties. A complete understanding of this interface is crucial in developing robust atmospheric chemical models and transmission of diseases via aerosols.

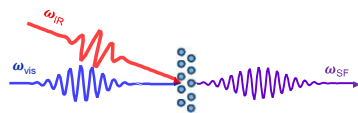
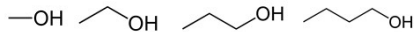


Figure 2. Schematic of VSFS from aerosol surfaces.

Vibrational sum frequency generation is an interface-specific technique since second-order nonlinear processes are forbidden from centrosymmetric media. The gas/aerosol particle interface breaks any such symmetry. The electric field of the sum frequency signal is proportional to analyte number density at the surface.

$$E_{\omega_{SF}} \propto N_s$$



Experiments

Experimental Set-up for Measurement of Aerosol Surfaces

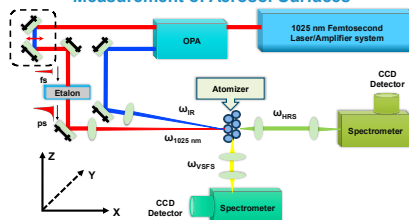


Figure 3. A 100kHz, 1025 nm laser is used to pump an OPA which produces a tunable IR pulse. A translation stage controls temporal overlap of the two incident pulses and an etalon converts the fs pulse to a ps pulse, providing a spectral resolution of 8 cm⁻¹. The incident pulses are focused and overlapped in space and time upon a stream of aerosol particles, forming an incident plane parallel to the optical table (XY-plane).

Results and Conclusions

Aerosol Particle Size Distribution

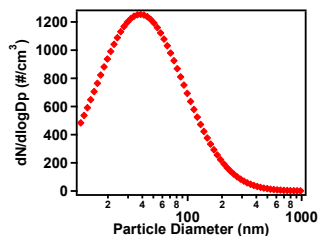


Figure 4. Aerosols at 4 L min⁻¹ produced from a particle generator have a density of 3.8 × 10⁶ cm⁻³ and size centered at 40 nm.

VSFS and HRS Spectra of Ethanol from Aerosol Particles

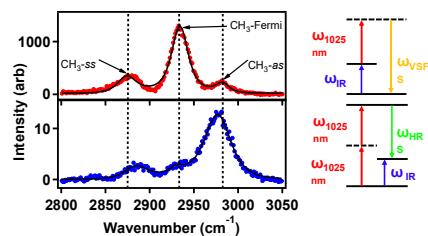


Figure 5. Vibrational spectra of 10 M ethanol in 0.5 M NaCl seed solution. The VSFS spectrum (top) shows the CH₃ symmetric stretch, Fermi resonance, and asymmetric stretching modes at 2879.7, 2932.8, and 2981.3 cm⁻¹, respectively. The bottom panel contains the corresponding HRS spectrum from the aerosol particle bulk phase.

Concentration Dependence of VSFS and HRS

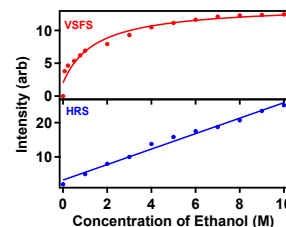


Figure 6. Intensity of the VSFS CH₃-Fermi peak at 2932.8 cm⁻¹ (top) and HRS CH₃-Fermi peak at 2930.1 cm⁻¹ (bottom) versus concentration of ethanol in the seed solution. The HRS signal is linearly correlated with bulk concentration as expected while the VSFS signal follows a Langmuir-type trend, corroborating that the VSFS signal is indeed from the gas/aerosol particle interface.

Polarized VSFS Spectra of Ethanol

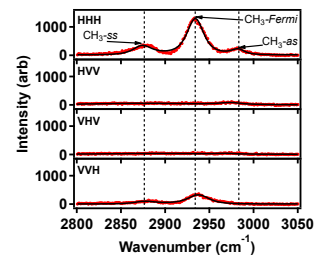


Figure 7. Polarization-resolved sum frequency can inform interfacial molecular orientation information. The lack of vibrational signatures fat HHV and VHV polarizations along with the discrete vibrational modes under HHH and VVH polarizations indicate that the ethanol molecules at the gas/aerosol particle interface are situated in an ordered fashion.

VSFS spectra of C=1-4 n-Alcohols

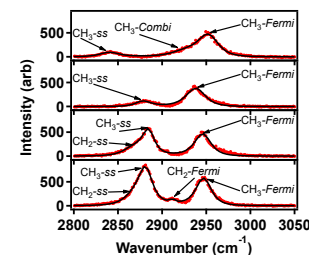


Figure 8. VSFS spectra collected at VVH polarization allow characterization of methanol, ethanol, 1-propanol, and 1-butanol (from top to bottom) at the gas/aerosol particle interface.

Surface Adsorption Free Energies of Ethanol to Air/Liquid and Gas/Aerosol Particle Interfaces

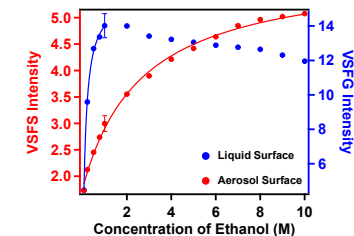


Figure 9. Concentration isotherm comparison of the gas/aerosol particle and air/liquid interfaces for 0-10 M ethanol in 0.5 M NaCl, observing CH₃-as electric fields from VSFS (red, left axis) and VSFG (blue, right axis) at HHH polarizations. The VSFG signal quickly reaches a maximum at 1 M ethanol and begins to decrease whereas the VSFS intensity increases gradually with ethanol concentration following a Langmuir-type trend.

$$E_{SF} \propto \frac{N_s}{N_{\infty}} \propto \frac{Kc}{Kc + 55.5}$$

$$\Delta G_{ads} = -RT \ln K$$

Surface Affinity of Ethanol

	Aerosol Particle	Planar Surface
K	21.04 ± 1.96	517.23 ± 90.40
ΔG_{ads} (kJ mol ⁻¹)	-7.55 ± 0.0001	-15.49 ± 0.0002

Summary

- We have demonstrated direct observation and characterization of organic species at and below the gas/aerosol particle interface through vibrational sum frequency and hyper-Raman scattering techniques.
- The highly curved nature of aerosol particles (diameter <50 nm) decreases the surface adsorption rate of organics compared to the planar liquid surface.

References

- Kolb, C.E. and D.R. Worsnop, *Annu Rev Phys Chem*, 2012, **63**: p. 471-491.
- Nozière, B.; Baduel, C.; Jaffrezou, J.-L., *Nat Comm*, 2014, **5**,(3335).
- Wang, H.-F.; Gan, W.; Lu, R.; Rao, Y.; Wu, B.-H., *Int'l Rev Phys Chem*, 2005, 2005, **24**: p. 191-256.
- de Beer, A. G.; Roke, S., *J Chem Phys*, 2010, **132**(234702).

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