5AC.11

Organosulfates Are Primarily Deprotonated at Atmospheric Aerosol Acidities: pH-Dependent Protonation State via Raman and Infrared Spectroscopy. ALISON FANKHAUSER, Ziying Lei, Kimberly Daley, Yao Xiao, Zhenfa Zhang, Avram Gold, Bruce Ault, Jason Surratt, Andrew Ault, University of Michigan Secondary organic aerosol (SOA) is a significant component of atmospheric fine particulate matter (PM2.5) globally that can form through multiphase chemistry of oxidized volatile organic compounds (VOC) leading to lower-volatility particulate species. Condensed phase reactions of certain SOA constituents with inorganic sulfate derived from SO_2 oxidation will lead to the formation of organosulfates, which can account for up to 10 – 15% of the organic mass within PM2.5. Despite the ubiquitous presence of atmospheric fine particulate organosulfates, our fundamental understanding of the molecular structure of organosulfates is limited, including for 2-methyltetrol organosulfates (2-MTSs), which are typically the single most abundant organosulfates measured in PM2.5, formed from isoprene oxidation products. As atmospheric aerosol pH varies widely (0 – 6), it is important to know whether organosulfates exist primarily in their protonated ($ROSO_3H$) or deprotonated ($ROSO_3^-$) forms. In this study, vibrational modes of synthetically pure 2-MTSs were spectroscopically probed using Raman and infrared (IR) spectroscopies, supported by density functional theory (DFT) of the protonated and deprotonated structures. Vibrational bands at 1035 and 1059 cm^{-1} were seen in both the IR and Raman spectra and were associated with the ROSO3- anion by comparison to DFT calculations. Analysis of Raman spectra across a range of acidities (pH = 0 – 10) shows that 2-MTSs are deprotonated ($ROSO_3^-$) at those pH values. Additional DFT calculations for organosulfates derived from isoprene, α-pinene, β-caryophyllene, and toluene suggest that most organosulfates exist in their deprotonated form ($ROSO_3^-$) in atmospheric particles. These charged species may have significant implications for our understanding of aerosol acidity and should be considered in thermodynamic model calculations.