Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information for

Raman Microspectroscopy and Vibrational Sum Frequency Generation Spectroscopy as Probes of the Bulk and Surface Compositions of Size-Resolved Sea Spray Aerosol Particles†

Andrew P. Ault[a‡], Defeng Zhao[b§‡], Carlena J. Ebben[c], Michael J. Tauber[b], Franz M. Geiger[c*], Kimberly A. Prather[b,d*], and Vicki H. Grassian[a*]

[a]Department of Chemistry, University of Iowa, Iowa City, Iowa, 52242, USA

[b]Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, 92093, USA.

[c]Department of Chemistry, Northwestern University, Evanston, Illinois, 60208, USA

[d]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California, 92093,USA.

[§] now at: Institute of Energy and Climate: Troposphere (IEK-8), Forschungszentrum Juelich, Juelich, D-52428, Germany

[‡]The first two authors contributed equally to this work.

† Electronic supplementary information (ESI) available.

Corresponding Authors: Franz M. Geiger, Kimberly A. Prather, and Vicki H. Grassian

E-mails: geigerf@chem.northwestern.edu, kprather@ucsd.edu, vicki-grassian@uiowa.edu

Raman/EDX Comparison. **Figure S1** shows the same particle analyzed with SEM-EDX in Figure 2 of the main text. The Raman data show the presence of vibrational modes due to sulfate, organics and water, with intensity in the ν(SO_4^{2-}) mode and the ν(C-H) and ν(O-H) modes, very similar to those observed in Figure 3 (see text for further details).

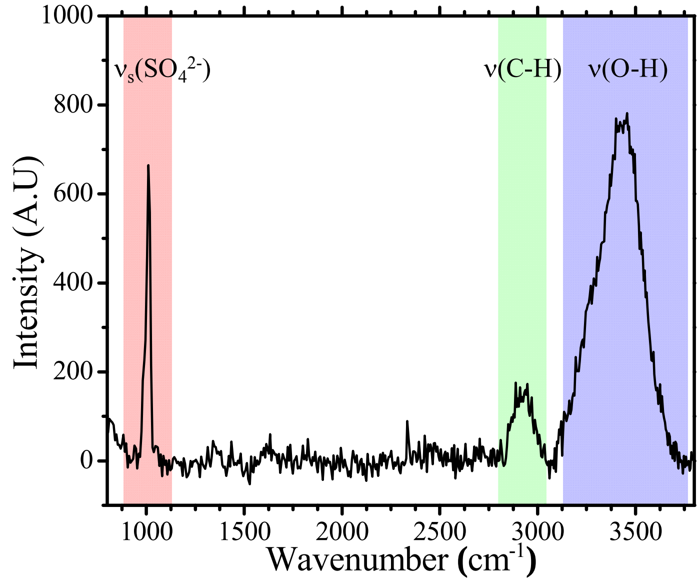

Figure S1. Raman spectrum of the same particle whose SEM image and energy spectra were shown in Figure 2.

Raman Spectra of Inorganic and Organic Reference Compounds. Sulfate and carbonate are two inorganic anion species present in seawater. $CaSO_4$ and Na_2SO_4 were selected as sulfate references and $CaCO_3$ as a carbonate reference. Figure S1 shows the frequency of the characteristic Raman peak of the symmetric stretch of sulfate ν(SO_4^{2-}) varies with different cations (Ca^{2+}/Na^{+}) and provides a potential way to differentiate these cations associated with sulfate.

The Raman peaks observed for $CaSO_4$ (1016 cm^{-1}),[3-4] Na_2SO_4 (995 cm^{-1}),[5-7] and $CaCO_3$ (1089 cm^{-1})[8-9] are similar to previously published values for these compounds.

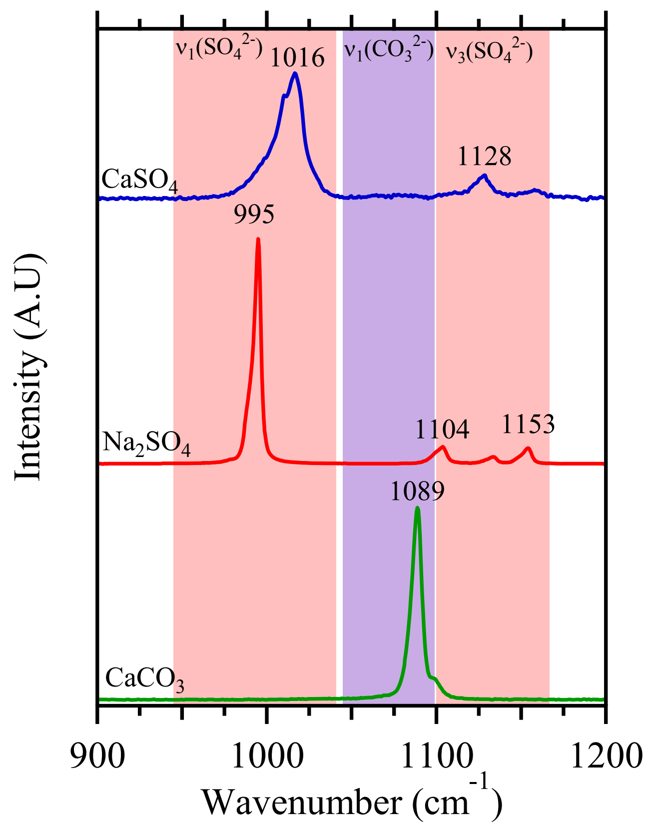

Figure S2. Raman spectra of inorganic reference compounds including $CaSO_4$ and Na_2SO_4 showing $\nu_1(SO_4^{2-})$ and $\nu_3(SO_4^{2-})$ modes, as well as $CaCO_3$ and the $\nu_1(CO_3^{2-})$ mode.

Table S1: Raman peak frequency of the symmetric stretch for sulfate in different compounds.

Salt	Peak frequency (cm^{-1})	References
Na_2SO_4	ν_1: 992.7	1
Na_2SO_4(aq)	ν_1: 982	2
K_2SO_4	ν_1: 983	10
$MgSO_4$	ν_1: 1022.8	11
$CaSO_4$	ν_1:1020	13
$CaSO_4 \cdot 0.5H_2O$	ν_1:1012;	14
$CaSO_4 \cdot 2H_2O$	ν_1: 1008	13

Organic reference compounds include sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$),[12] palmitic acid ($CH_3(CH_2)_{14}COOH$),[15] and glycine (NH_2CH_2COOH),[16-17] and lipopolysaccharides from *Escherichia Coli*.[18] These species contain some of the functional groups that are expected to have similar Raman signatures, as the main organic species in seawater including carbohydrates, lipids, carboxylic acids, peptides, and amines.[19-21] Figure S2 shows that among the organic reference compounds studied here, the symmetric/asymmetric stretching modes of the CH, CH_2, and CH_3 groups exhibit the most intense Raman signals.

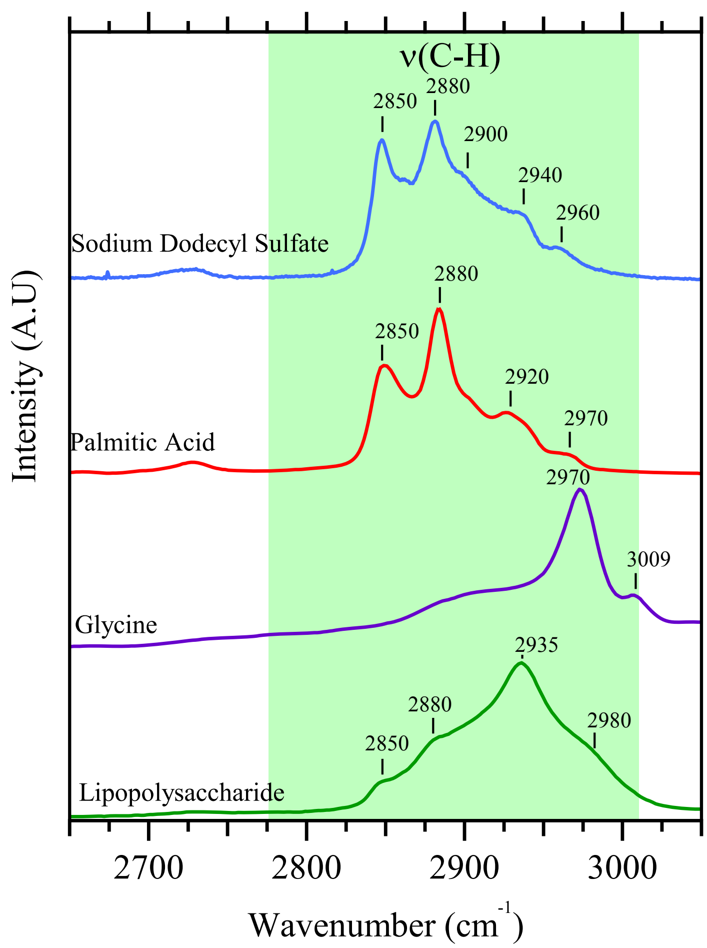

Figure S3. Raman spectra in the C-H stretching region are shown for different organic standards (Sodium Dodecyl Sulfate – $CH_3(CH_2)_{11}OSO_3Na$, Palmitic Acid – $CH_3(CH_2)_{14}COOH$, Glycine – NH_2CH_2COOH, Lipopolysaccharides from *Escherichia Coli*)

Raman Spectra of Different Particle Types. Figure S3 shows roughly 20 representative spectra (normalized) from MOUDI stages 1-5 from before the addition of biogenic material. A transition from spectra dominated by the $\nu(SO_4^{2-})$ and ν(O–H) modes for large particles to spectra dominated by the ν(C–H) modes for small particles can be observed in Figure S3.

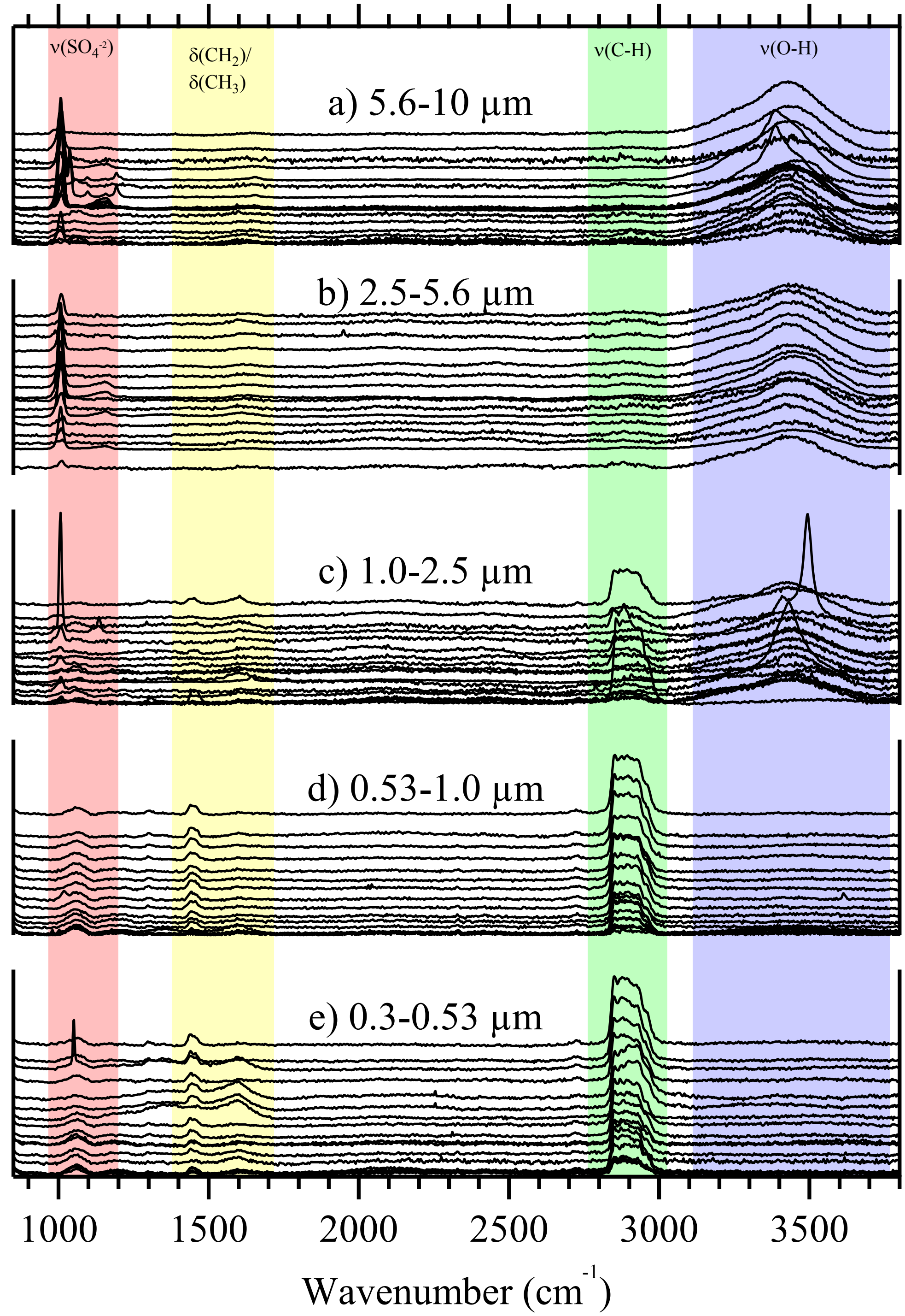

Figure S4. Approximately 20 Raman spectra from single particles on different MOUDI stages, a) 5.6-10.0 µm, b) 2.5-5.6 µm, c) 1.0-2.5 µm, d) 0.53-1.0 µm, e) 0.3-0.53 µm.

Supplementary Information References

1. Choi, B. K.; Lockwood, D. J., *Solid State Commun* **1989,** *72* (1), 133-137.
2. Daly, F. P.; Kester, D. R.; Brown, C. W., *J. Phys. Chem.* **1972,** *76* (24), 3664-&.
3. Berenblut, B. J.; Dawson, P.; Wilkinson, G. R., *Spectroc. Acta Pt. A-Molec. Spectr.* **1973,** *29* (1), 29-36.
4. Jentzsch, P. V.; Bolanz, R. M.; Ciobota, V.; Kampe, B.; Rosch, P.; Majzlan, J.; Popp, J., *Vib. Spectrosc.* **2012,** *61*, 206-213.
5. Tong, H. J.; Reid, J. P.; Dong, J. L.; Zhang, Y. H., *J. Phys. Chem. A* **2010,** *114* (46), 12237-12243.
6. Fung, K. H.; Tang, I. N., *Appl. Spectrosc.* **1991,** *45* (5), 734-737.
7. Murugan, R.; Ghule, A.; Chang, H., *J. Phys.: Condens. Matter* **2000,** *12* (5), 677-700.
8. Gunasekaran, S.; Anbalagan, G.; Pandi, S., *J. Raman Spectrosc.* **2006,** *37* (9), 892-899.
9. Andersen, F. A.; Brecevic, L., *Acta Chem. Scand.* **1991,** *45* (10), 1018-1024.
10. Ishigame, M.; Yamashita, S., *Phys Status Solidi B* **1983,** *116* (1), 49-56.
11. Wang, A.; Freeman, J. J.; Jolliff, B. L.; Chou, I. M., *Geochim. Cosmochim. Acta* **2006,** *70* (24), 6118-6135.
12. Picquart, M., *J. Phys. Chem.* **1986,** *90* (2), 243-250.
13. Prasad, P. S. R.; Pradhan, A.; Gowd, T. N., *Curr. Sci.* **2001,** *80* (9), 1203-1207.
14. Xiao, H. S.; Dong, J. L.; Wang, L. Y.; Zhao, L. J.; Wang, F.; Zhang, Y. H., *Environ. Sci. Technol.* **2008,** *42* (23), 8698-8702.
15. De Gelder, J.; De Gussem, K.; Vandenabeele, P.; Moens, L., *J. Raman Spectrosc.* **2007,** *38* (9), 1133-1147.
16. Zhu, G. Y.; Zhu, X.; Fan, Q.; Wan, X. L., *Spectroc. Acta Pt. A-Molec. Spectr.* **2011,** *78* (3), 1187-1195.
17. Takeda, M.; Iavazzo, R. E. S.; Garfinkel, D.; Scheinberg, I. H.; Edsall, J. T., *J. Am. Chem. Soc.* **1958,** *80* (15), 3813-3818.
18. Kamnev, A. A.; Tarantilis, P. A.; Antonyuk, L. P.; Bespalova, L. A.; Polissiou, M. G.; Colina, M.; Gardiner, P. H. E.; Ignatov, V. V., *J. Mol. Struct.* **2001,** *563*, 199-207.
19. Aluwihare, L. I.; Repeta, D. J., *Mar. Ecol.: Prog. Ser.* **1999,** *186*, 105-117.
20. Verdugo, P.; Alldredge, A. L.; Azam, F.; Kirchman, D. L.; Passow, U.; Santschi, P. H., *Mar. Chem.* **2004,** *92* (1-4), 67-85.
21. Gibb, S. W.; Mantoura, R. F. C.; Liss, P. S., *Global Biogeochem. Cycles* **1999,** *13* (1), 161-177.