

Supporting Information:

***In Situ* Mass Spectrometric Detection of Interfacial Intermediates in the Oxidation of RCOOH(aq) by Gas-Phase OH-Radicals**

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SI Text

Since mass spectrometers detect net charge, the first step is the separation of pre-existing anions from cations in the inflowing solutions.^{1,2}

1- We have demonstrated experimentally that the charges we detect are largely produced pneumatically by showing that ion signals (i) increase at higher gas velocities v_g and (ii) extrapolate to zero as $v_g \rightarrow 0$.²

2- We have confirmed that the modest polarizations of the microjets do not affect the observed chemistries³⁻⁸ by showing that the kinetics of the reaction of dissolved α -tocopherol with gaseous ozone determined on the basis of negative and positive ion detection were identical.⁶

3- Since the nebulizer gas can fragment the first generation microdroplets but not the smaller charged droplets for hydrodynamic reasons,^{9,10} the creation of net charge is a one-time event.

4- Second generation microdroplets may lose mass via solvent evaporation in the dry $N_2(g)$ atmosphere, but retain their excess charges. We have verified that the net charge carried by the ensemble of microdroplets is proportional to the concentrations of the reactant, intermediates and products formed on the surface of the jet during reactive gas-liquid collisions.

5- The concentration dependences observed in present and previous experiments strongly support our assumption that the detected species are indeed produced on the surface of the intact jet containing microdroplets ($D_0 > 1 \mu m$) (whose composition is identical to that of the injected solution) rather than on the ensemble of daughter droplets (whose compositions span the broad distributions generated by random solvent evaporation).^{3-5,11} This finding corroborates previous reports showing

that the titration curves of carboxylic acids and trimethylamine obtained from the dependence of the carboxylate and trimethylammonium mass spectrometric signals as functions of pH in this setup are identical to those determined by standard titrations in the injected solutions, both leading to the ionization constants reported in the literature, i.e., $pK_a = 4.8$ and 9.8 , respectively.^{3,4}

6- A key feature of our instrument is that the jet issuing from the nozzle source is orthogonal to the polarized inlet to the mass spectrometer. Therefore, the charged droplets deflected toward the mass spectrometer preferentially originate from the interfacial layers of the jet, while its core maintains its forward trajectory. The ejection of dissolved ions to the gas-phase takes place from the smallest droplets at the end of a sequence of events comprising extensive solvent evaporation, and net charge crowding in shrinking droplets that become unstable and undergo a cascade of Coulomb explosions.^{12,13} Finally, gas-phase ions are sorted out and detected by the online mass spectrometer.

7- The possibility that the species we monitor were produced in the reactions of gases with the highly concentrated, high surface-to-volume small droplets undergoing Coulomb explosions is excluded by experimental evidences. We had found that product signal intensities *decrease* (rather than increase) by injecting the reactive gases 5 mm and 10 mm downstream (relative to the standard position of the gas injector) along the jet direction.¹⁴ This is the expected outcome of a process in which products are formed in collisions of the reactive gases with the intact jet. The fact that product formation is not completely suppressed by shifting the gas injector downstream is ascribed to the fact that the gas beams lose their collimation by turbulent mixing with the nebulizer gas at the reaction zone.

8- Previous data analysis based on mass balances and the kinetic theory of gases¹⁵ suggested that the thickness of the interfacial layers sampled in these experiments is less than one nm.^{4,16} More compellingly, we recently showed that the depth of the interfacial layers sampled in our experiments is controllable as a function of nebulizer gas velocity v_g .² Under the present high v_g (~ 160 m/s) condition, anions that reside at the topmost layers of the air–water interface are preferentially detected as mass signals.²

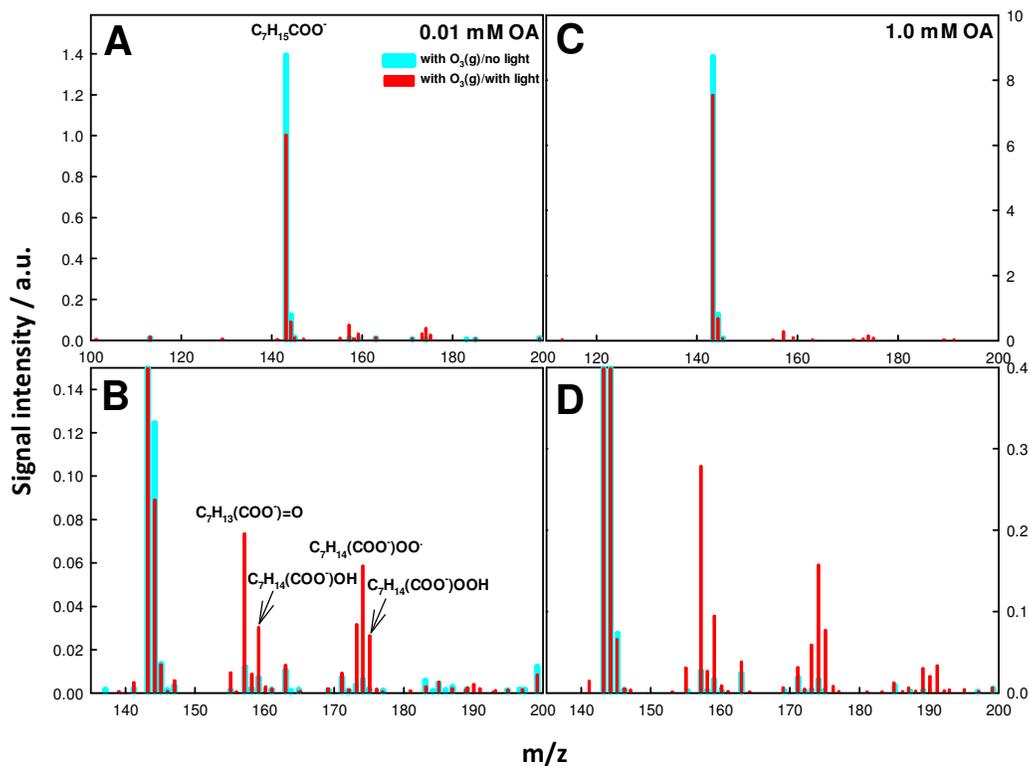


Figure S1 Negative ion electrospray mass spectra of 0.01 mM (pH 5.6) (A, B) or 1.0 mM (pH 3.7) (C, D) octanoic acid microjets exposed to 570 or 600 ppmv $O_3(g)$, respectively, in $O_2(g)/H_2O(g)/N_2(g)$ mixtures at 1 atm and 298 K. Cyan: laser off. Red: under 40 mJ, ~ 8 ns pulses (at 10 Hz) of 266 nm radiation. $1 \text{ ppmv} = 2.46 \times 10^{13} \text{ molecules cm}^{-3}$.

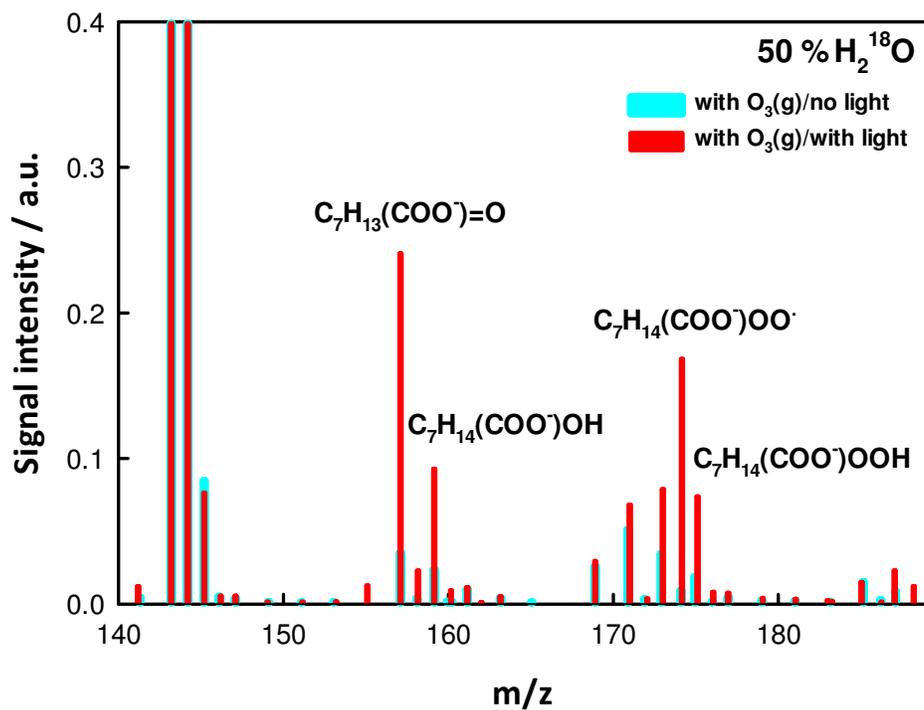


Figure S2 Negative ion electrospray mass spectra of 2.5 mM octanoic acid in 50 vol% H₂¹⁸O microjets exposed to 610 ppmv O₃(g)/O₂(g)/H₂O(g)/N₂(g) mixtures at 1 atm and 298 K. Cyan: laser off. Red: under 40 mJ, ~ 8 ns pulses (at 10 Hz) of 266 nm radiation ($[\cdot OH]_0 \sim 60$ ppmv). 1 ppmv = 2.46×10^{13} molecules cm⁻³.

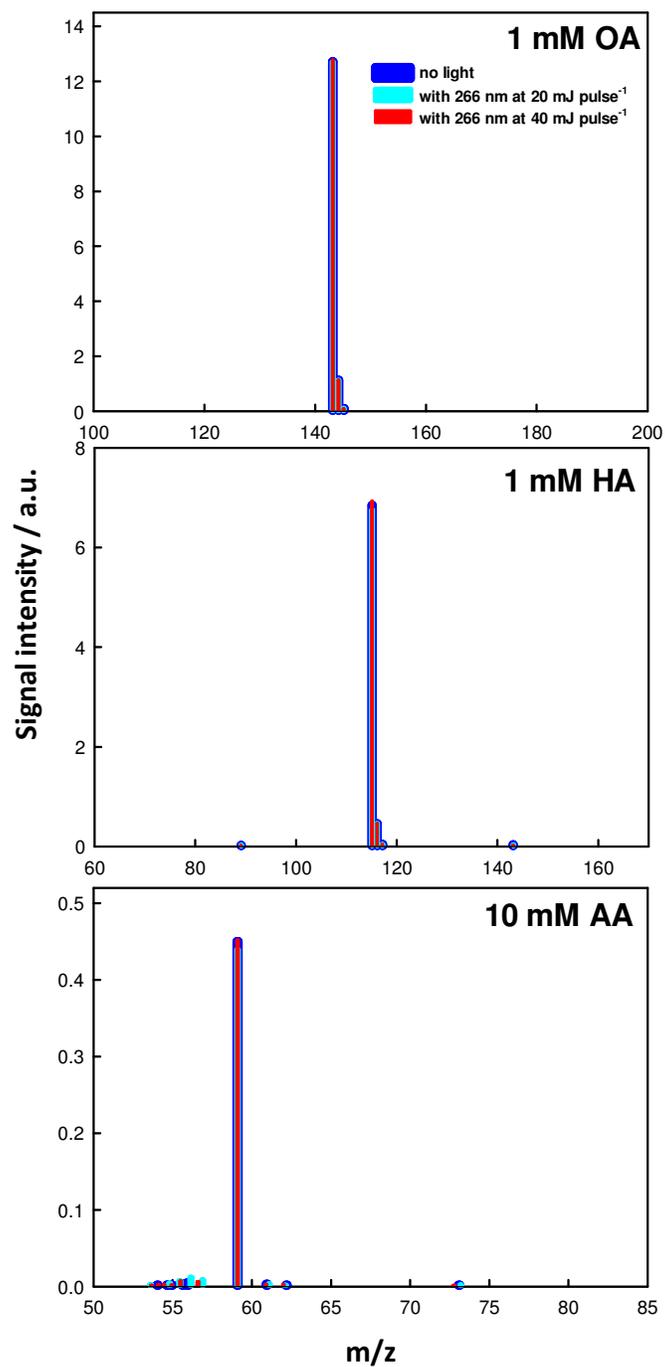


Figure S3 Negative ion electrospray mass spectra of 1 mM octanoic acid, 1 mM hexanoic acid, and 10 mM acetic acid microjets in the absence (blue)/presence (cyan, red) of 266 nm laser beam irradiation under just N₂ atmosphere.

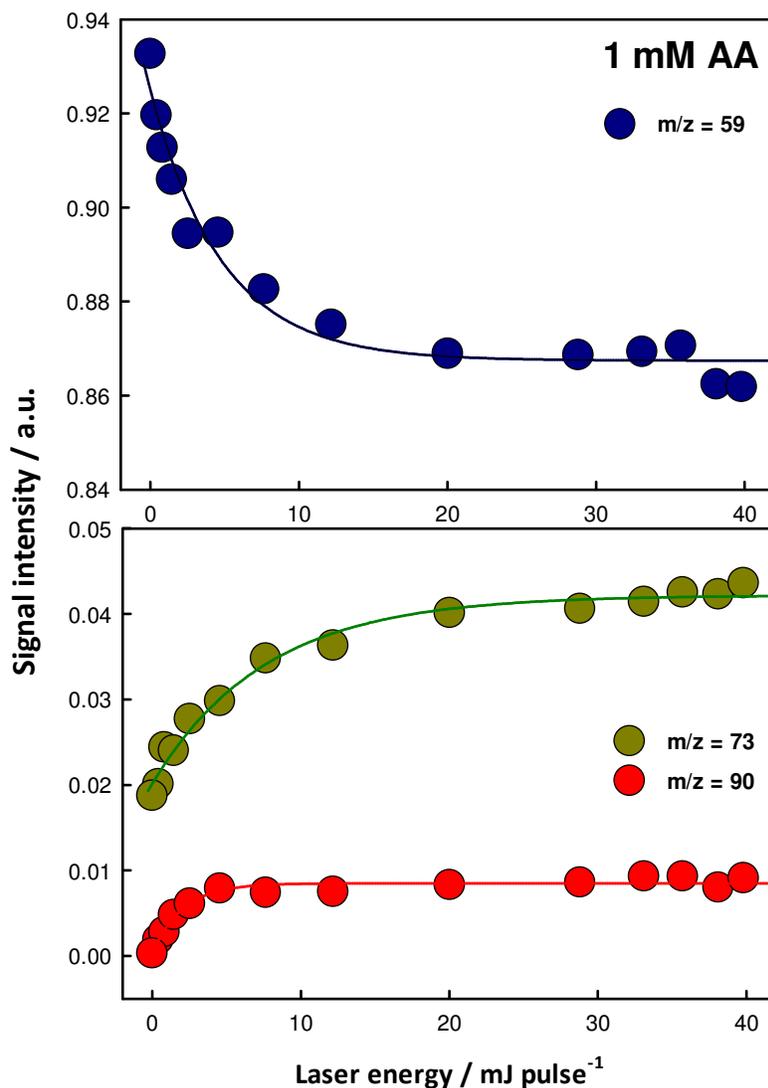


Figure S4 Electro spray mass spectral signal intensities from aqueous 1 mM (pH 3.7) acetic acid microjets exposed to $\text{O}_3(\text{g})/\text{O}_2(\text{g})/\text{H}_2\text{O}(\text{g})/\text{N}_2(\text{g})$ mixtures at $[\text{O}_3(\text{g})] \sim 610$ ppmv irradiated by 266 nm laser beams for $\sim 10\text{-}50 \mu\text{s}$ contact times as a function of laser energy mJ pulse^{-1} . Laser energies (x-axis) at 1, 5, 10, 20, 30, and 40 mJ pulse^{-1} correspond to $[\cdot\text{OH}]_0 \approx 2, 10, 18, 34, 47$ and 58 ppmv, respectively. $1 \text{ ppmv} = 2.46 \times 10^{13} \text{ molecules cm}^{-3}$. The m/z = 59 (CH_3COO^-), 73 ($\text{CH}(\text{COO}^-)=\text{O}$), and 90 ($\text{CH}_2(\text{COO}^-)\text{OO}\cdot$).

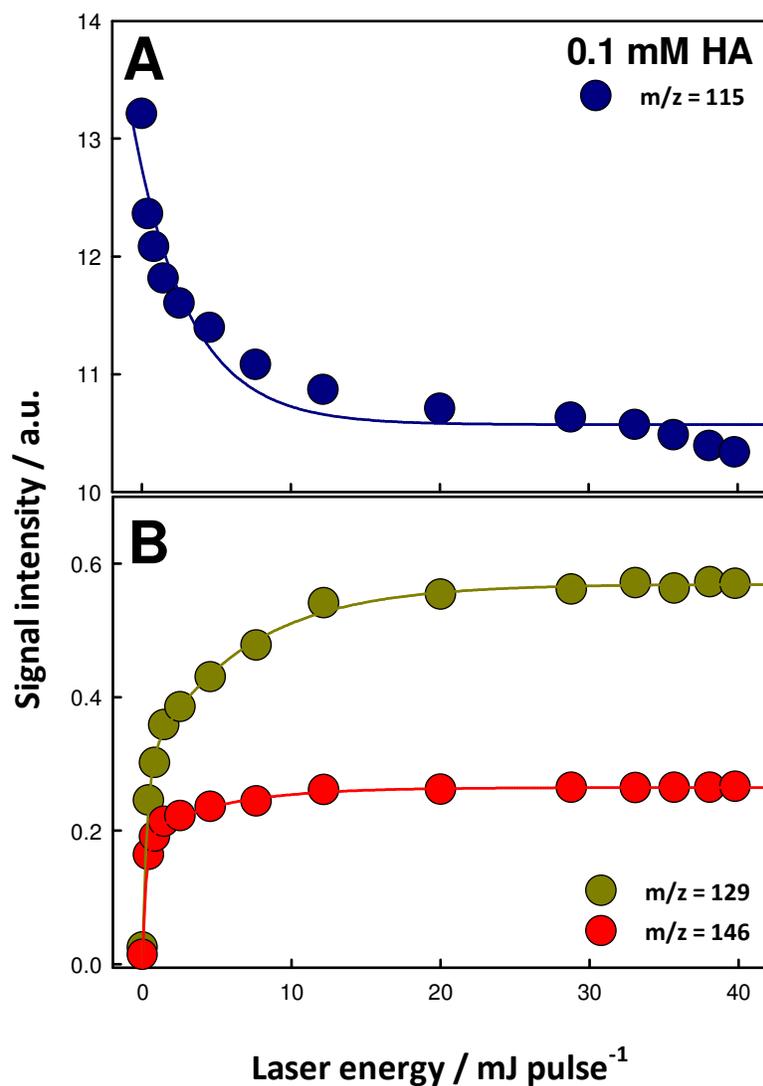


Figure S5 Electro spray mass spectral signal intensities from aqueous 0.1 mM (pH 4.8) hexanoic acid microjets exposed to $O_3(g)/O_2(g)/H_2O(g)/N_2(g)$ mixtures at $[O_3(g)] \sim 610$ ppmv irradiated by 266 nm laser beams for ~ 10 -50 μs contact times as a function of laser energy MJ pulse^{-1} . Laser energies (x-axis) at 1, 5, 10, 20, 30, and 40 MJ pulse^{-1} correspond to $[\cdot OH]_0 \approx 2, 10, 18, 34, 47$ and 58 ppmv, respectively. 1 ppmv = 2.46×10^{13} molecules cm^{-3} . The $m/z = 115$ ($C_5H_{11}COO^-$), 129 ($C_5H_9(COO^-)=O$), and 146 ($C_5H_{10}(COO^-)OO\cdot$).

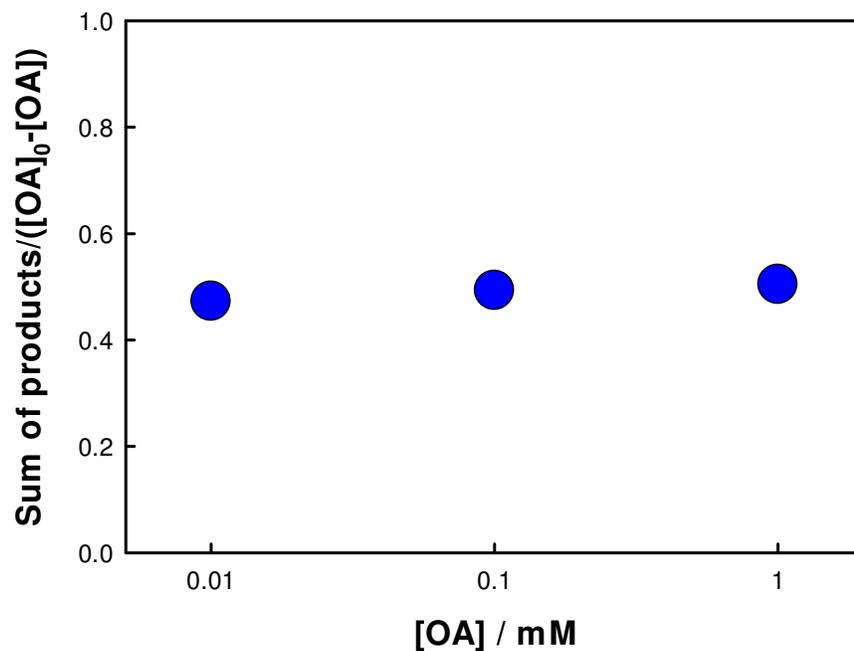


Figure S6 Total mass signal intensities of formed products, including the carbonyl, alcohol, peroxy radical, and peroxide, were divided by the loss of octanoate, $[OA]_{\text{without}266\text{nm}} - [OA]_{\text{with}266\text{nm}}$ at $[O_3(g)] = 570\sim 640$ ppmv. Laser energy was 40 mJ pulse^{-1} ($[^{\cdot}\text{OH}]_0 \approx 54\sim 61$ ppmv)

SI REFERENCES

- (1) Enami, S.; Colussi, A. J. Long-Range Hofmeister Effects of Anionic and Cationic Amphiphiles. *J. Phys. Chem. B* **2013**, *117*, 6276-6281.
- (2) Enami, S.; Colussi, A. J. Long-Range Specific Ion-Ion Interactions in Hydrogen-Bonded Liquid Films. *J. Chem. Phys* **2013**, *138*, 184706.
- (3) Mishra, H.; Enami, S.; Nielsen, R. J.; Stewart, L. A.; Hoffmann, M. R.; Goddard, W. A.; Colussi, A. J. Bronsted Basicity of the Air-Water Interface. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 18679-18683.
- (4) Enami, S.; Hoffmann, M. R.; Colussi, A. J. Proton Availability at the Air/Water Interface. *J. Phys. Chem. Lett.* **2010**, *1*, 1599-1604.
- (5) Enami, S.; Hoffmann, M. R.; Colussi, A. J. Acidity Enhances the Formation of a Persistent Ozonide at Aqueous Ascorbate/Ozone Gas Interfaces. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 7365-7369.
- (6) Enami, S.; Hoffmann, M. R.; Colussi, A. J. How Phenol and Alpha-Tocopherol React with Ambient Ozone at Gas/Liquid Interfaces. *J. Phys. Chem. A* **2009**, *113*, 7002-7010.
- (7) Enami, S.; Vecitis, C. D.; Cheng, J.; Hoffmann, M. R.; Colussi, A. J. Electrospray Mass Spectrometric Detection of Products and Short-Lived Intermediates in Aqueous Aerosol Microdroplets Exposed to a Reactive Gas. *J. Phys. Chem. A* **2007**, *111*, 13032-13037.
- (8) Enami, S.; Sakamoto, Y.; Colussi, A. J. Fenton Chemistry at Aqueous Interfaces. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 623-628.
- (9) Lasheras, J. C.; Villermaux, E.; Hopfinger, E. J. Break-up and Atomization of a Round Water Jet by a High-Speed Annular Air Jet. *J Fluid Mech* **1998**, *357*, 351-379.
- (10) Gorokhovski, M. A.; Saveliev, V. L. Analyses of Kolmogorov's Model of Breakup and Its Application into Lagrangian Computation of Liquid Sprays under Air-Blast Atomization. *Phys Fluids* **2003**, *15*, 184-192.
- (11) Mishra, H.; Enami, S.; Nielsen, R. J.; Hoffmann, M. R.; Goddard, W. A.; Colussi, A. J. Anions Dramatically Enhance Proton Transfer through Water Interfaces. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 10228-10232.
- (12) Iribarne, J. V.; Thomson, B. A. On the Evaporation of Small Ions from Charged Droplets. *J. Chem. Phys.* **1976**, *64*, 2287.
- (13) Kebarle, P.; Peschke, M. On the Mechanisms by Which the Charged Droplets Produced by Electrospray Lead to Gas Phase Ions. *Anal. Chim. Acta* **2000**, *406*, 11.

(14) Enami, S.; Vecitis, C. D.; Cheng, J.; Hoffmann, M. R.; Colussi, A. J. Global Inorganic Source of Atmospheric Bromine. *J. Phys. Chem. A* **2007**, *111*, 8749-8752.

(15) Davidovits, P.; Kolb, C. E.; Williams, L. R.; Jayne, J. T.; Worsnop, D. R. Mass Accommodation and Chemical Reactions at Gas-Liquid Interfaces. *Chem. Rev.* **2006**, *106*, 1323-1354.

(16) Enami, S.; Stewart, L. A.; Hoffmann, M. R.; Colussi, A. J. Superacid Chemistry on Mildly Acidic Water. *J. Phys. Chem. Lett.* **2010**, *1*, 3488-3493.