

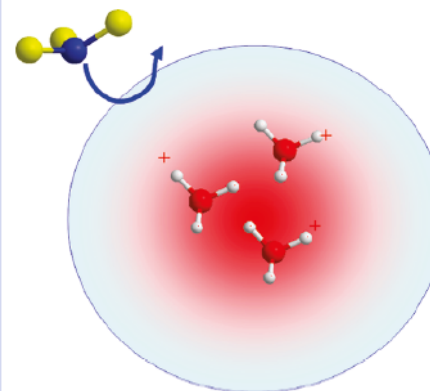
Proton Availability at the Air/Water Interface

Shinichi Enami, Michael R. Hoffmann, and A. J. Colussi*

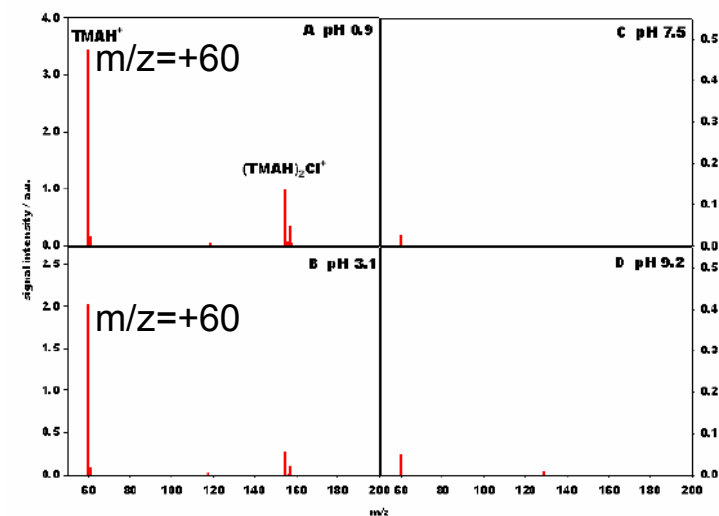
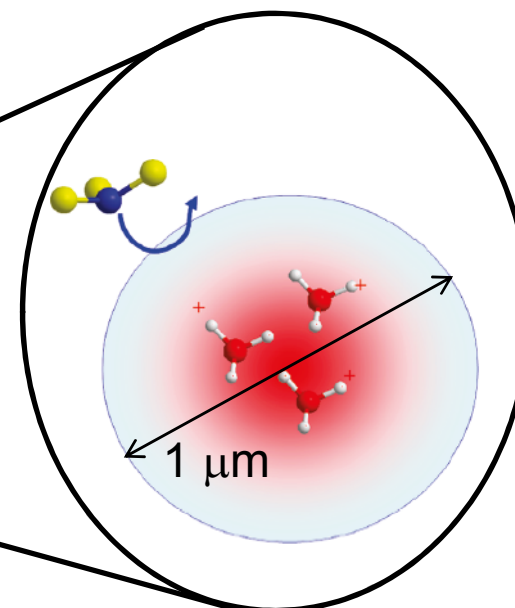
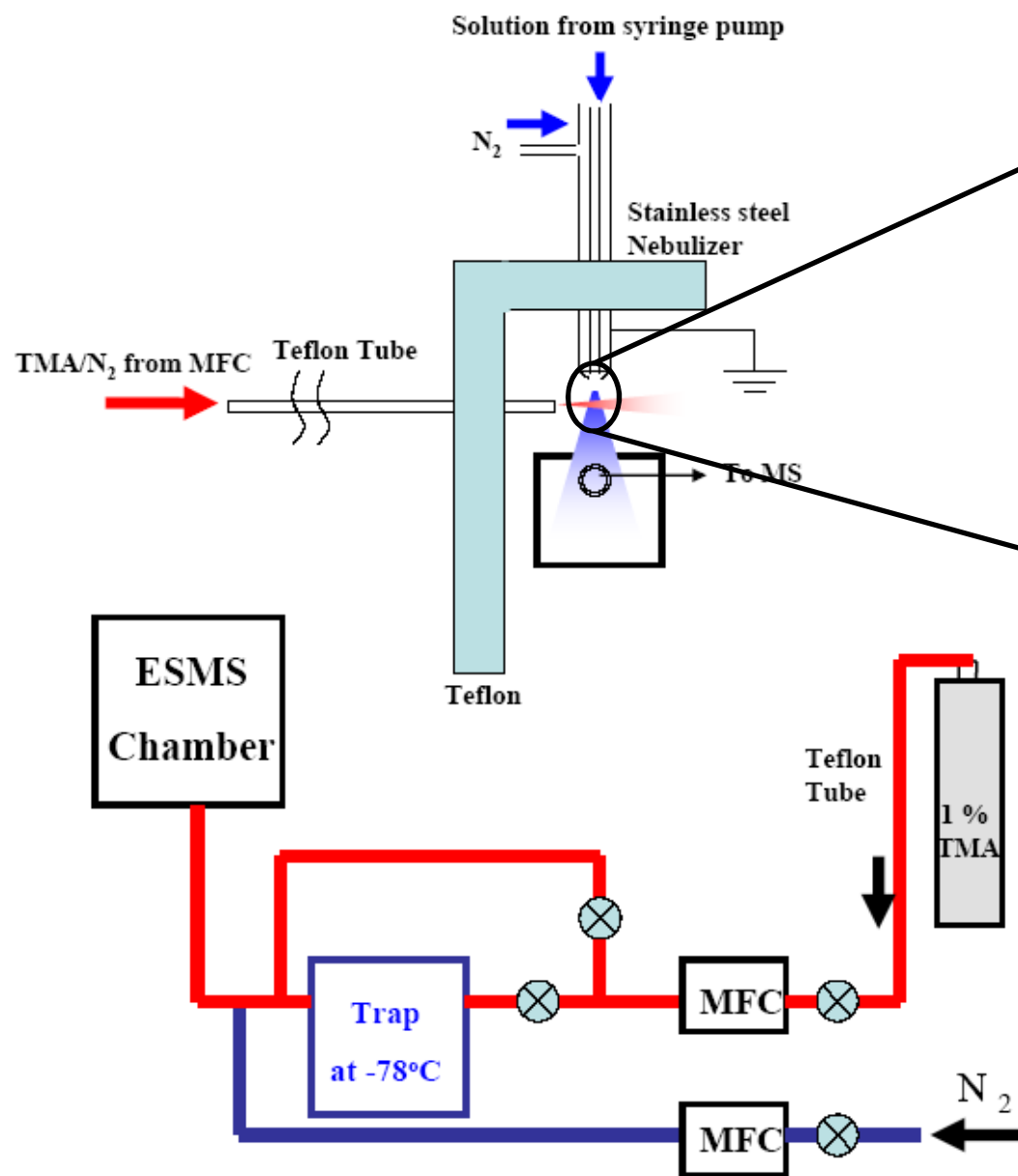
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ABSTRACT The acidity of the water surface sensed by a colliding gas is determined in experiments in which the protonation of gaseous trimethylamine (TMA) on aqueous microjets is monitored by online electrospray mass spectrometry as a function of the pH of the bulk liquid (pH_{BLK}). TMAH⁺ signal intensities describe a titration curve whose equivalence point at pH_{BLK} 3.8 is dramatically smaller than the acidity constant of trimethylammonium in bulk solution, $\text{p}K_{\text{A}}(\text{TMAH}^+) = 9.8$. Notably, the degree of TMA protonation above pH_{BLK} 4 is enhanced hundred-fold by submillimolar LiCl or NaCl and weakly inhibited at larger concentrations. Protonation enhancements are associated with the onset of significant direct kinetic solvent hydrogen isotope effects. Since TMA(g) can be protonated by H₂O itself only upon extensive solvent participation, we infer that H₃O⁺ emerges at the surface of neat water below pH_{BLK} 4.

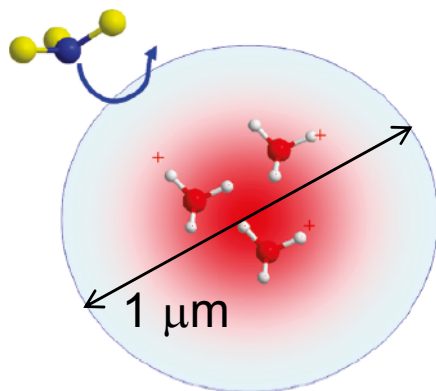
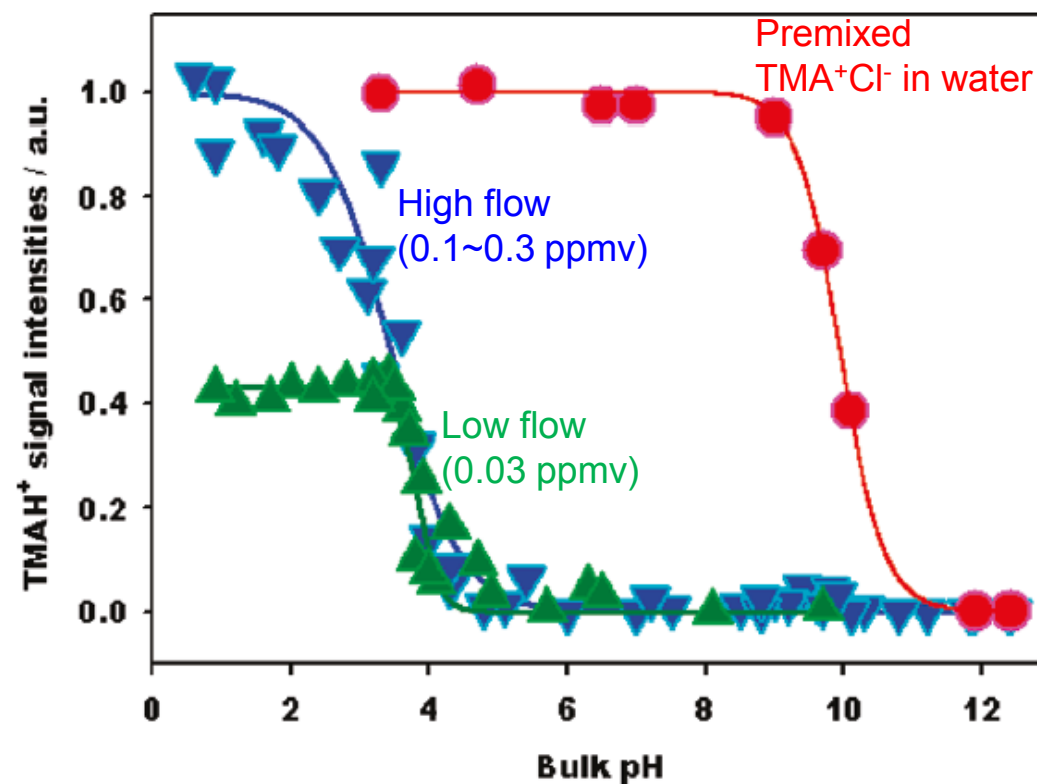
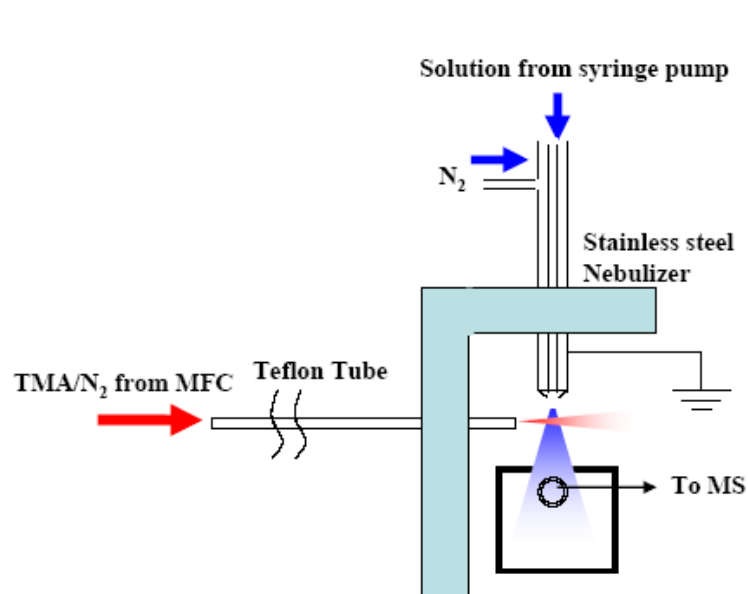
SECTION Atmospheric, Environmental and Green Chemistry



Setup - Electrospray ionization mass spectrometer (ESI-MS)

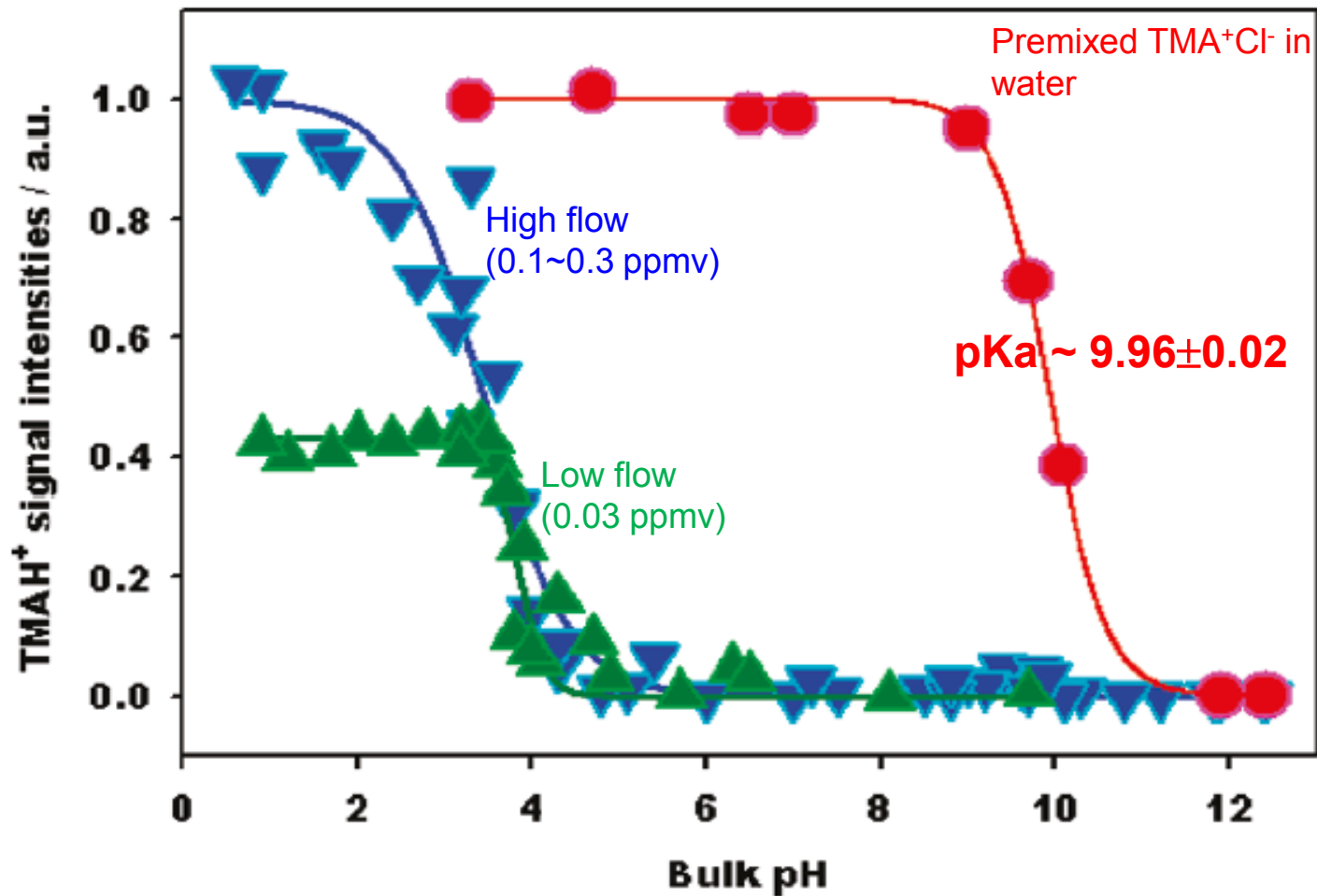


Experiment – TMA/N₂ collide with water droplet



➡ Amine senses less proton when it touches interfacial region of microdroplets.

Experiment – TMA/N₂ collide with water droplet



$$\frac{[A^-]}{[A]_T} = \frac{1}{1 + 10^{pK_A - pH_{BLK}}}$$

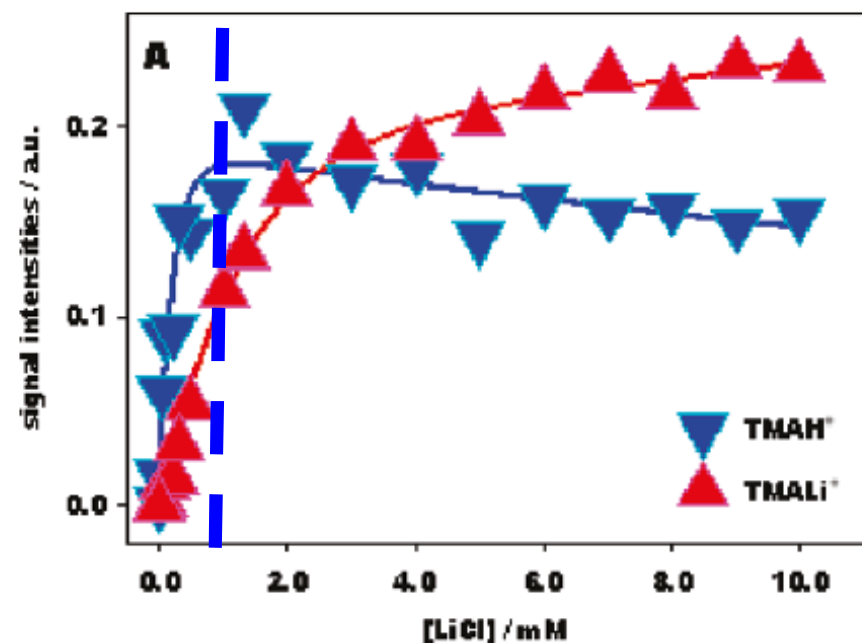
(3)

In colliding TMA(g) to water droplet



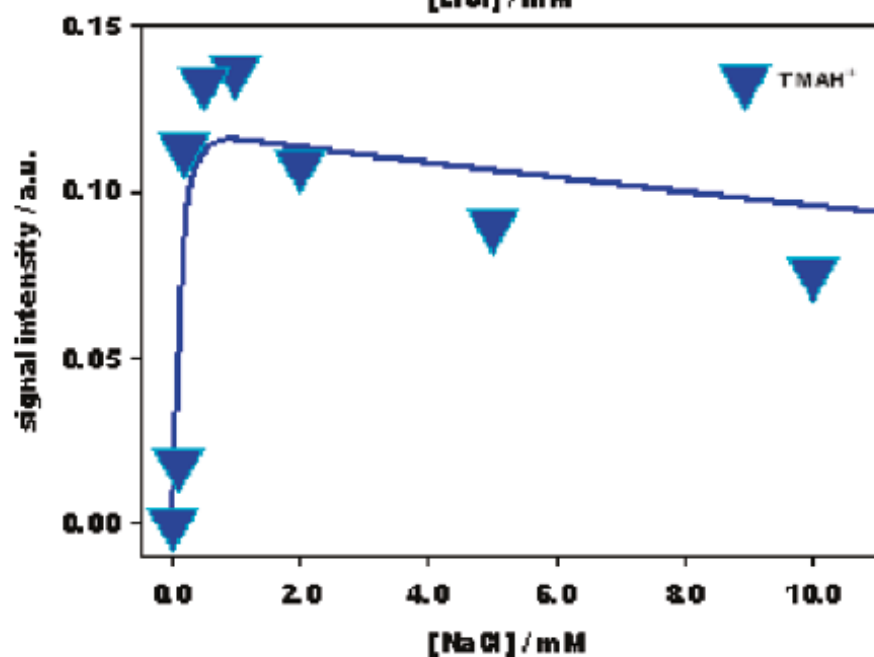
Effective pKa ~ 3.8 ± 0.2.

System - Electrospray ionization mass spectrometer (ESI-MS)



→ TMAH⁺ signal drastically increases with insertion of LiCl (or NaCl) in the water droplets.

→ Maximum intensity at ~ 1 mM.



Perhaps not coincidentally, LiCl and NaCl enhance TMA protonation (Figure 2) in the same concentration range in which the surface tension of aqueous electrolytes dips to a minimum (the Jones–Ray effect).^{8,23,24} Since the Debye screening length is > 3 nm at the onset of electrolyte effects at 0.1 mM (Figure 2),²⁵ both phenomena seem to manifest short-range forces associated with the local structure of interfacial water.^{26–29} It could tentatively be argued that Li⁺ and Na⁺ replace protons as counterions in the diffuse electric double layer,²⁵ thereby releasing them to the surface.³⁰ Alternative explanations are being explored experimentally in our laboratory.

What is Jones-Ray effect?

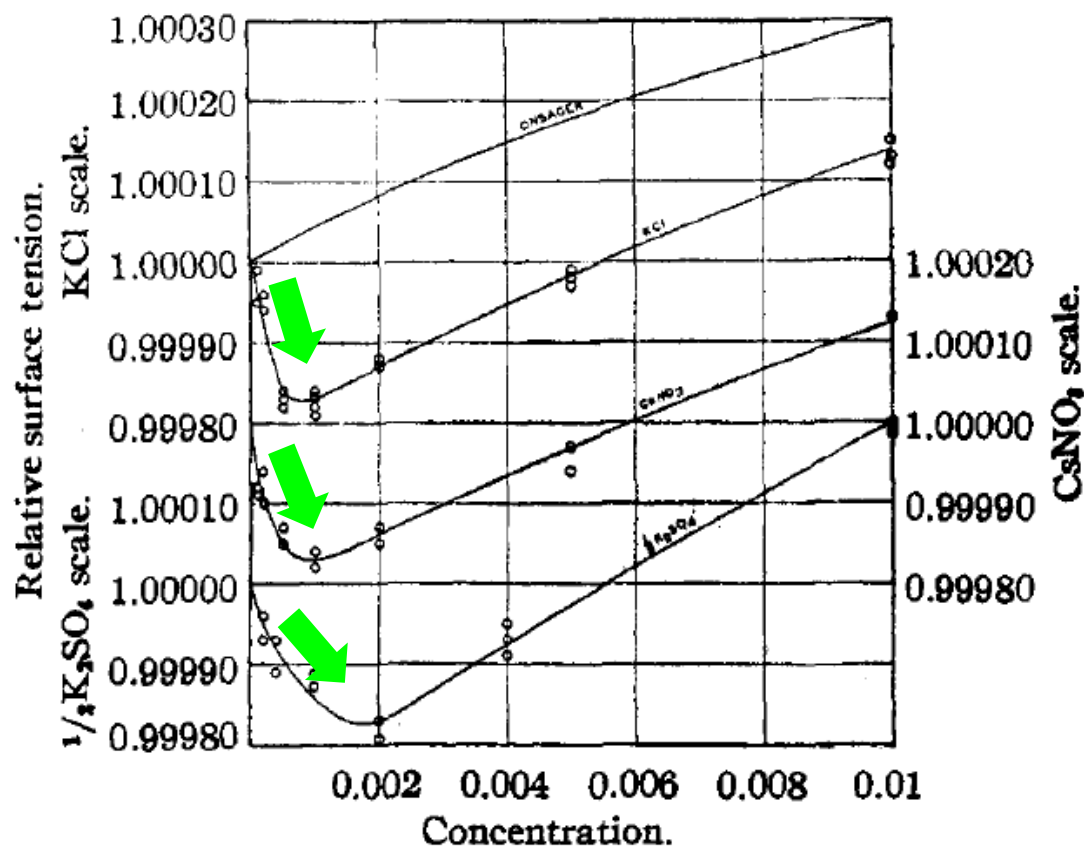


Fig. 2. *JACS.* 1937, 59, 187.

- Very small decreases of surface tension was measured.
- Tried to understand by preferential solute adsorption at air/water interface.

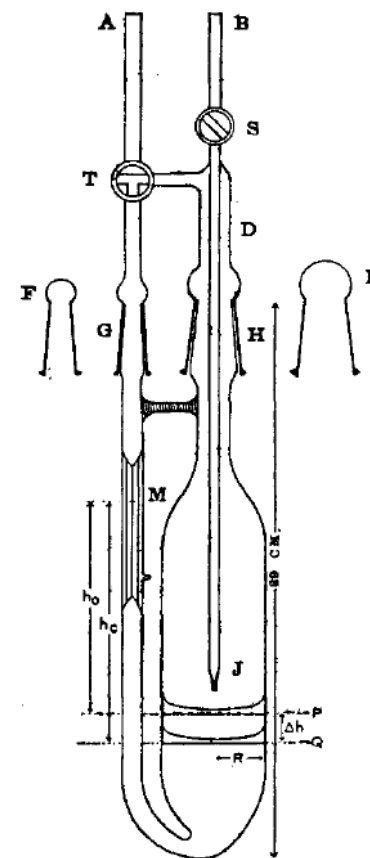
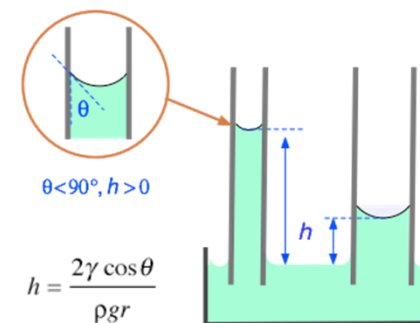
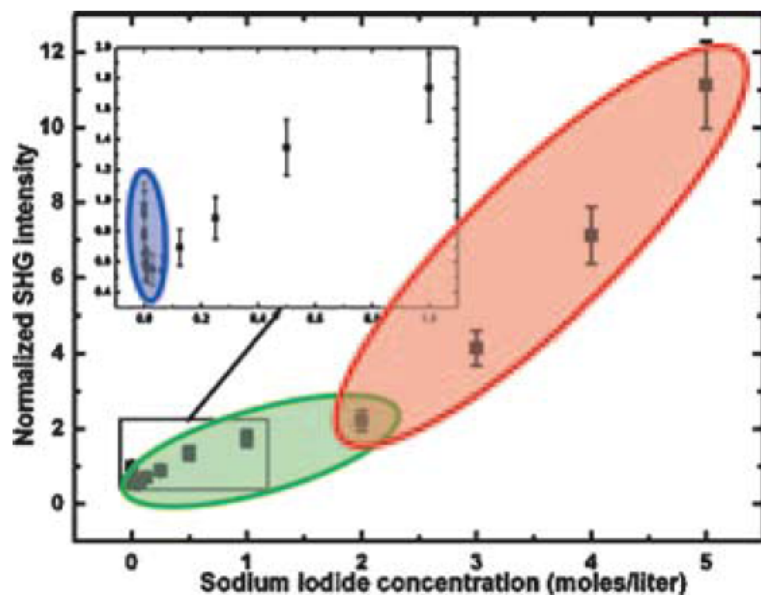


Fig. 1.—Silica capillarimeter.



*Recent reinvestigation on Jones-Ray effect

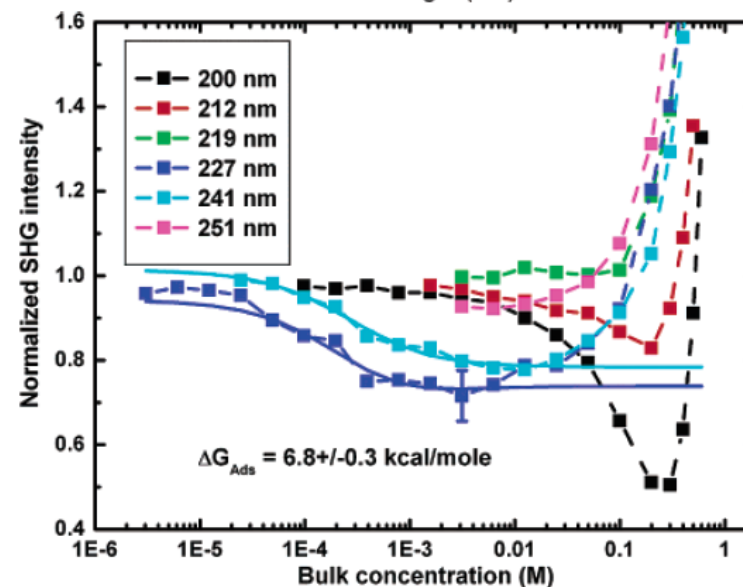
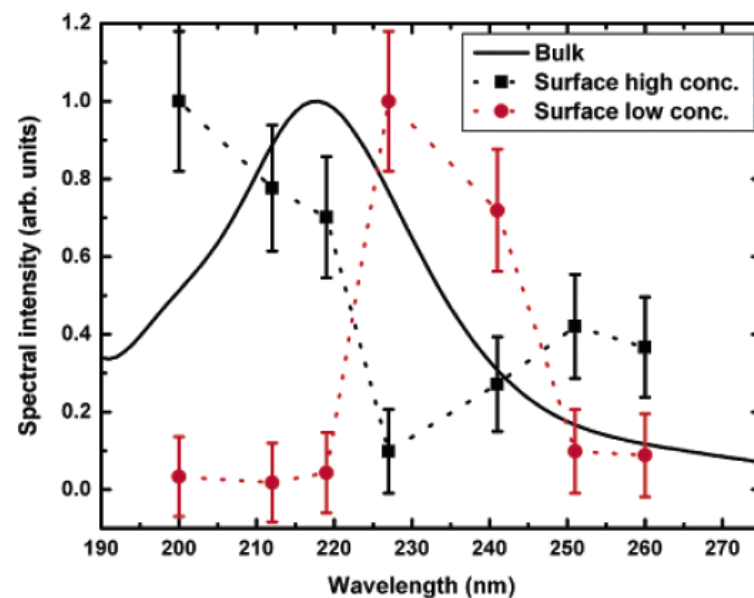


$$I_{2\omega} \propto |\chi^{(2)}|^2 I_{\omega}^2 \quad (1)$$

$$\chi^{(2)} = \chi_{\text{water}}^{(2)} + \chi_{\text{anion}}^{(2)} \quad (2)$$

Petersen and Saykally, *Annu. Rev. Phys. Chem.* **2006**, 57, 333.

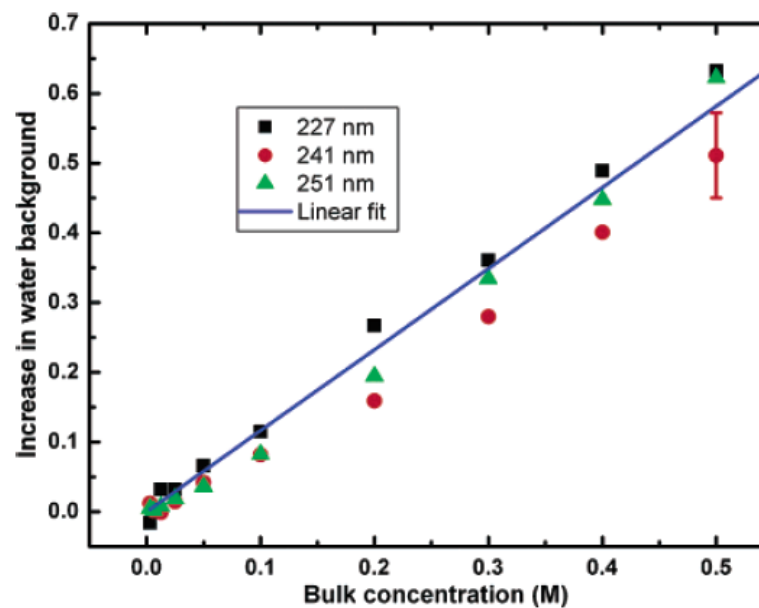
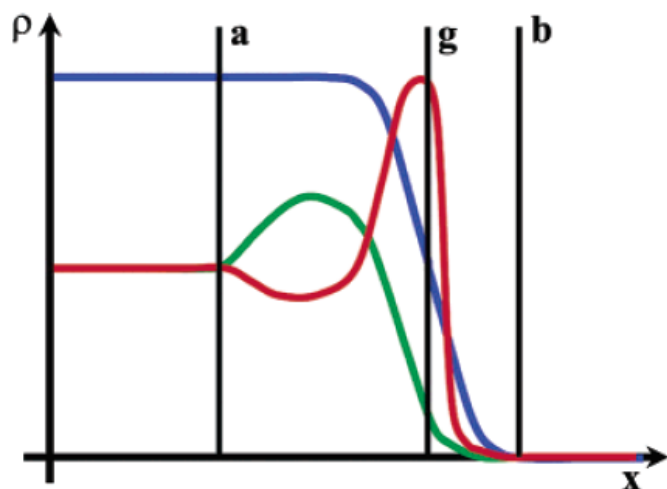
Technique: monitoring resonant surface SHG from solvated I⁻ by CTTS.



Petersen and Saykally, *JACS.* **2005**, 127, 15446.

*Recent reinvestigation on Jones-Ray effect

$$N_s = \frac{N_s^{\max} \times KC}{C_w + KC} \approx \frac{N_s^{\max} \times C}{C + 55.5M \times \exp(\Delta G_{\text{Ads}}/RT)} \quad (3)$$



Petersen and Saykally, *JACS*. **2005**, 127, 15446.

Gibbs free energy
of adsorption of -6.8 ± 0.3 kcal/mol.

pH and TMA flow dependence of protonation.

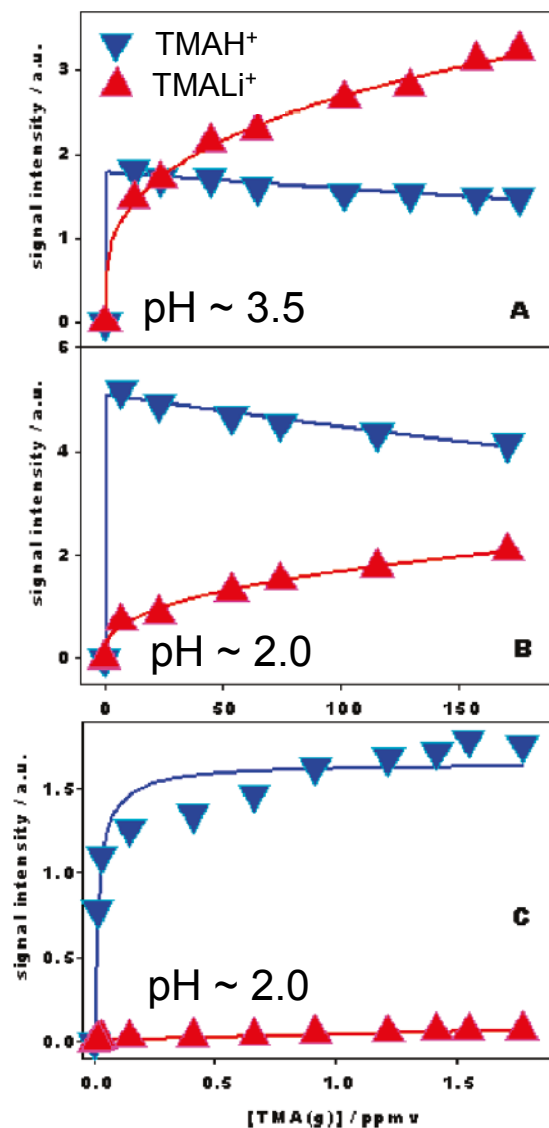
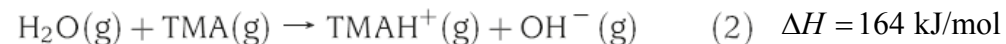
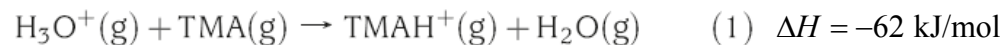


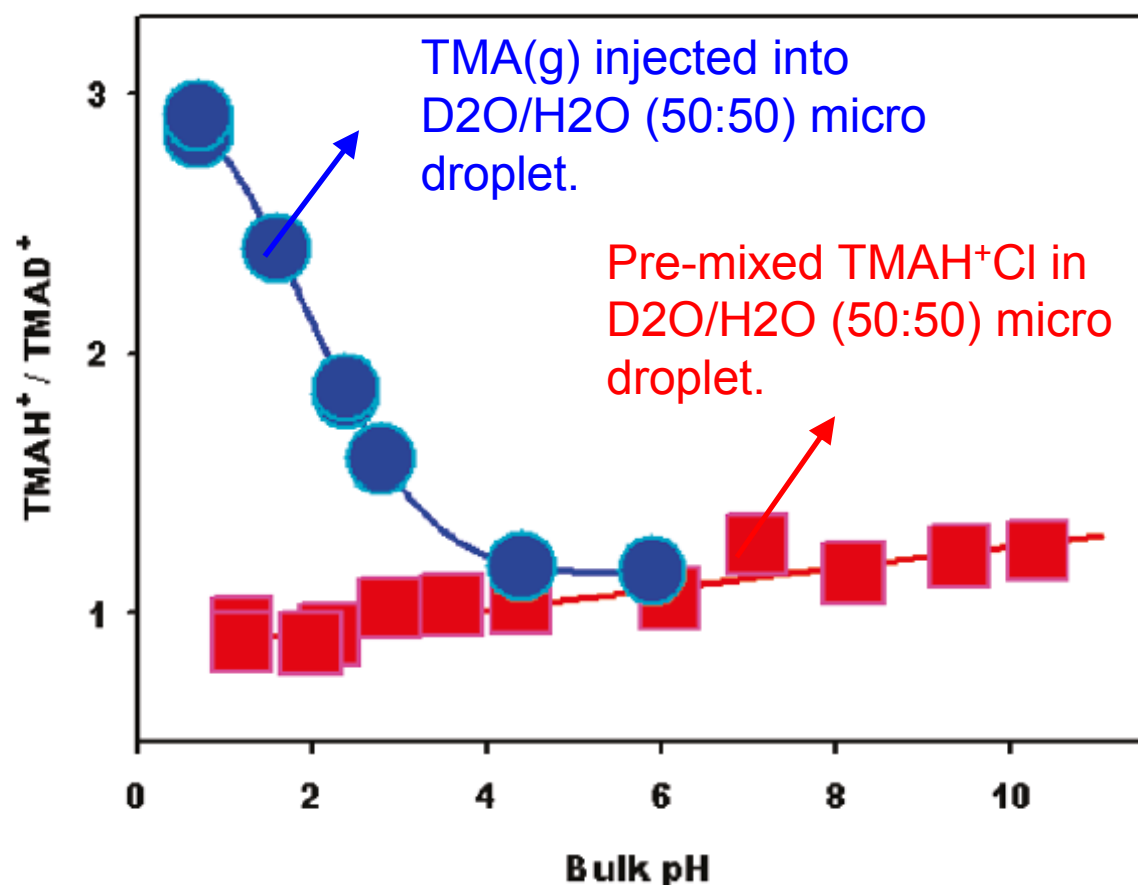
Figure 3. ESI-MS TMAH⁺ ($m/z = 60$, blue downward triangles) and TMALi⁺ ($m/z = 66$, red upward triangles) signal intensities on 100 mM aqueous LiCl microjets at (A) $\text{pH}_{\text{BLK}} 3.5$ and (B and C) $\text{pH}_{\text{BLK}} 2.0$, as functions of [TMA(g)].



➡ TMAH⁺ signal increases in low bulk pH.

jets. Since the limiting TMAH⁺ signal intensities reached under 0.03 ppmv TMA(g) are only 43 % of those obtained at ~100 times larger TMA(g) number densities (at $\text{pH}_{\text{BLK}} < 3$; Figure 1), uptake is limited by TMA(g) in the former case and by interfacial protons above 1.0 ppmv TMA(g). This finding is corroborated by the observation that TMAH⁺ signals plateau above ~0.3 ppmv TMA(g) at $\text{pH}_{\text{BLK}} 2.0$, while TMALi⁺ signals keep increasing at larger TMA(g) concentrations (Figure 3C). Since the partial depletion of TMA near the air/water interface should have affected both TMAH⁺ and TMALi⁺ signals, the observed behaviors exclude significant resistance from gas-phase diffusion to TMA(g) uptake under present conditions. A limited role for gas-phase diffusion cannot be technically excluded, however, because all experiments were performed on aqueous microjets of similar dimensions under 1 atm of total pressure.

Isotope effect of protonation



➡ Amount of harvested TMAH⁺ is much larger than that of TMAD⁺ in the case of gas collision.

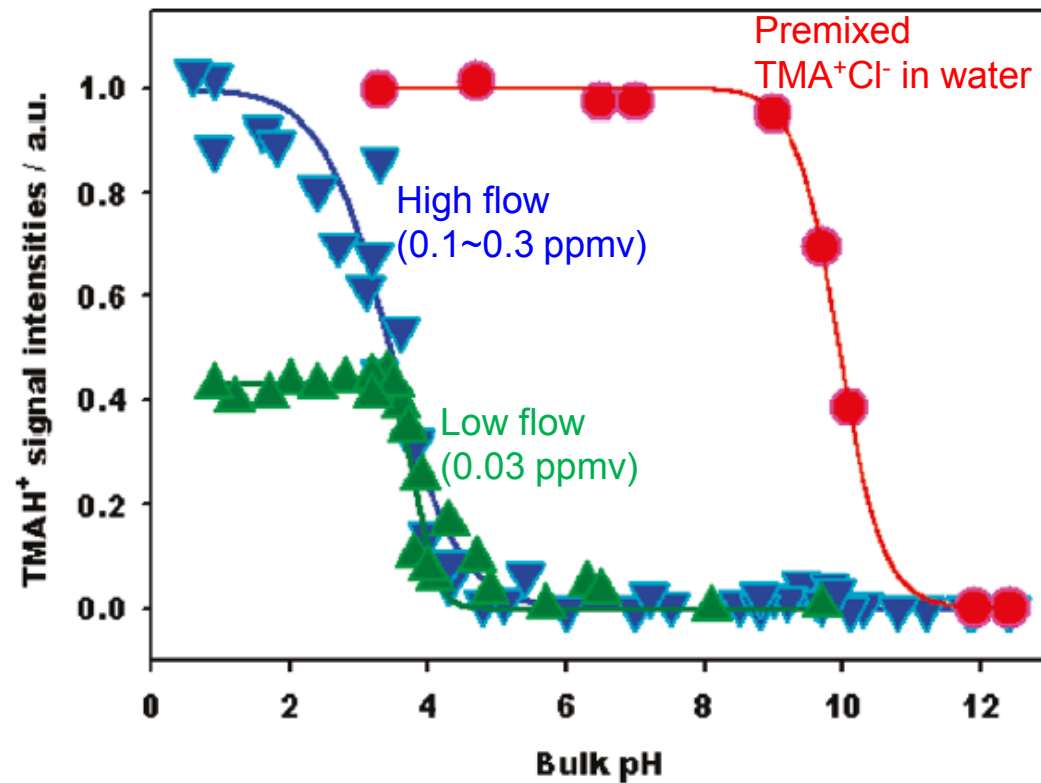
➡ Excess TMAH⁺ over TMAD⁺ is due to the difference in diffusion coefficient of D⁺ and H⁺.

Figure 4. The TMAH⁺ ($m/z = 60$)/TMAD⁺ ($m/z = 61$) ESI-MS signal ratio as a function of pH_{BLK} . Blue circles are from H₂O/D₂O (50:50) microjets exposed to 1 ppmv TMA(g). Red squares are from TMAH⁺Cl⁻ solutions in H₂O/D₂O (50:50).

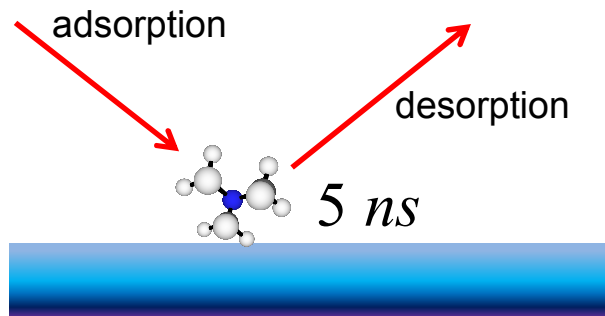
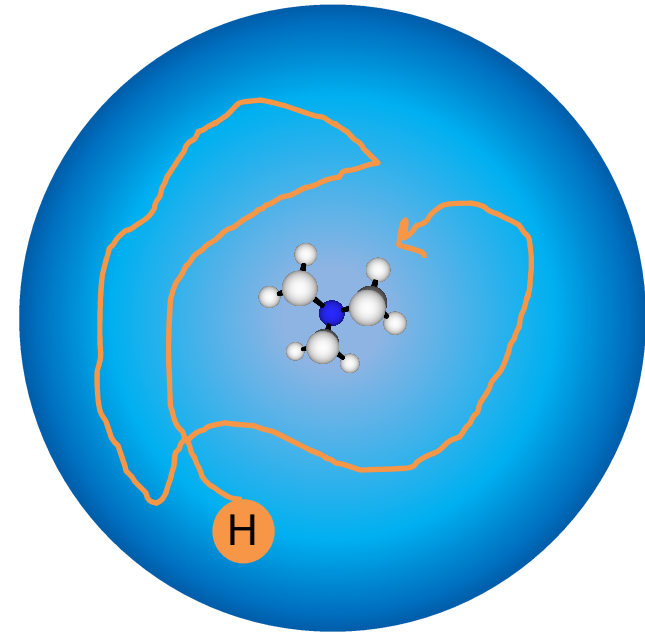
Isotope effect of protonation

We infer that (1) H/D are fully scrambled prior to analyzing TMAH^+Cl^- solutions in $\text{H}_2\text{O}/\text{D}_2\text{O}$ and (2) the enhanced TMA(g) protonation on water surfaces at $\text{pH}_{\text{BLK}} < 4$ and on Li^+/Na^+ solutions at $\text{pH}_{\text{BLK}} > 5$ is due to the faster protonation of adsorbed TMA molecules. Additional evidence that our experiments actually monitor interfacial chemical events follows from the $\text{TMAH}^+/\text{TMAD}^+ \approx 1/4$ ratio measured on neat D_2O microjets at $\text{pH}_{\text{BLK}} 3$, exposed to 1 ppmv TMA(g) humidified with ~ 250 ppmv $\text{H}_2\text{O(g)}$. A much smaller $\text{TMAH}^+/\text{TMAD}^+ < 1/40$ value should have been measured if incoming $\text{H}_2\text{O(g)}$ had undergone full H-isotope scrambling with microjet bulk D_2O .

Model – finite adsorption time vs diffusion limited reaction



Diffusion limited reaction



$$\left\{ \begin{array}{l} k_P = 4\pi(D_H + D_{TMA})R_{TMA+H^+}[H^+] \\ = 2 \times 10^7 \text{ s}^{-1} \\ \tau_D = 1/k_D < 1/(10k_P) \sim 5 \text{ ns} \end{array} \right.$$

Conclusion

- 1) Effective pKa value of adsorbed TMA is about 4 (bulk pKa ~10).
- 2) The authors suggested that finite time & diffusion of proton makes shift of pKa of amine group in TMA.
- 3) Insertion of salt (NaCl/LiCl) some enhances the protonation of TMA.
(Seems to follow Jones-Dole effect, but deeper discussions are not found.)
- 4) More TMAH⁺ emerges from the gas Collision than TMAD⁺ because of larger diffusion coefficient of H⁺.