

A (personal) laboratory perspective

- Snow or ice?
- How well do we understand “pristine” frozen water as a substrate?
 - Direct photochemistry; heterogeneous reactions; solute exclusion; acid deposition
- How about frozen salty water?
 - Direct photochemistry; heterogeneous reactions; acid deposition; sea ice chemistry



Sumi Wren



Tara Kahan

ACP - Special Issue: *New perspectives on Air-Ice Chemical Interactions (AICI)*

Editor(s): V. F. McNeill, E. Wolff, T. Bartels-Rausch, and H. Pfeiffenberger

Halogen activation via interactions with environmental ice and snow in the polar lower troposphere and other regions

J. P. D. Abbatt, et al [Atmos. Chem. Phys., 12, 6237-6271, 2012](#)

Organics in environmental ices: sources, chemistry, and impacts

V. F. McNeill, et al. [Atmos. Chem. Phys., 12, 9653-9678, 2012](#)

A compilation of tropospheric measurements of gas-phase and aerosol chemistry in polar regions

R. Sander and J. Bottenheim [Earth Syst. Sci. Data, 4, 215-282, 2012](#)

The role of the global cryosphere in the fate of organic contaminants

A. M. Grannas, et al., [Atmos. Chem. Phys., 13, 3271-3305, 2013](#)

Relationship between snow microstructure and physical and chemical processes

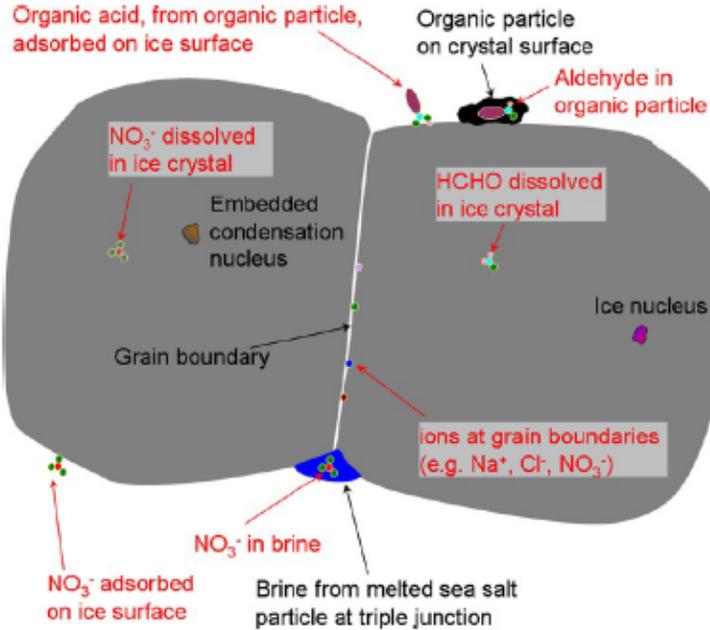
T. Bartels-Rauschet al., [Atmos. Chem. Phys. Discuss., 12, 30409-30541, 2012](#)

Can We Model Snow Photochemistry? Problems with the Current Approaches

Florent Domine,^{*,†,‡} Josué Bock,[§] Didier Voisin,[§] and D. J. Donaldson^{||}

- Fundamental assumption in snow (photo)chemistry is that some fraction of reactants are present in a “QLL”, and that reactions may be as though occurring in a true liquid.
- Is this a good (universal) approach?

oNO!



There are many regions where reagents may accumulate. These may present very different reaction environments and hence kinetics / photochemistry

Snow is not (sea) ice

The existence of an actual liquid layer on snow surface is unphysical

Formation and history of snow are important

Chemistry occurring within deposited or core organic particles may be

- important

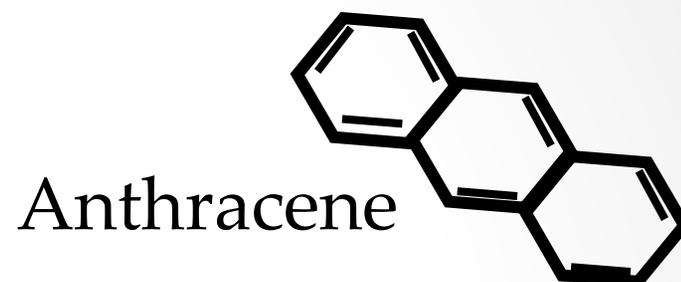
What is needed

Given all this complexity, it is plainly clear that today we are not able to produce a mechanistic snow chemistry model with a predictive capacity. This goal even seems elusive in the near future. Initial developments should logically be devoted to sites where the chemical composition is the least complicated, where extensive measurements can be made, and these field and modeling studies would ideally be complemented by well-designed laboratory experiments. The simplest natural systems

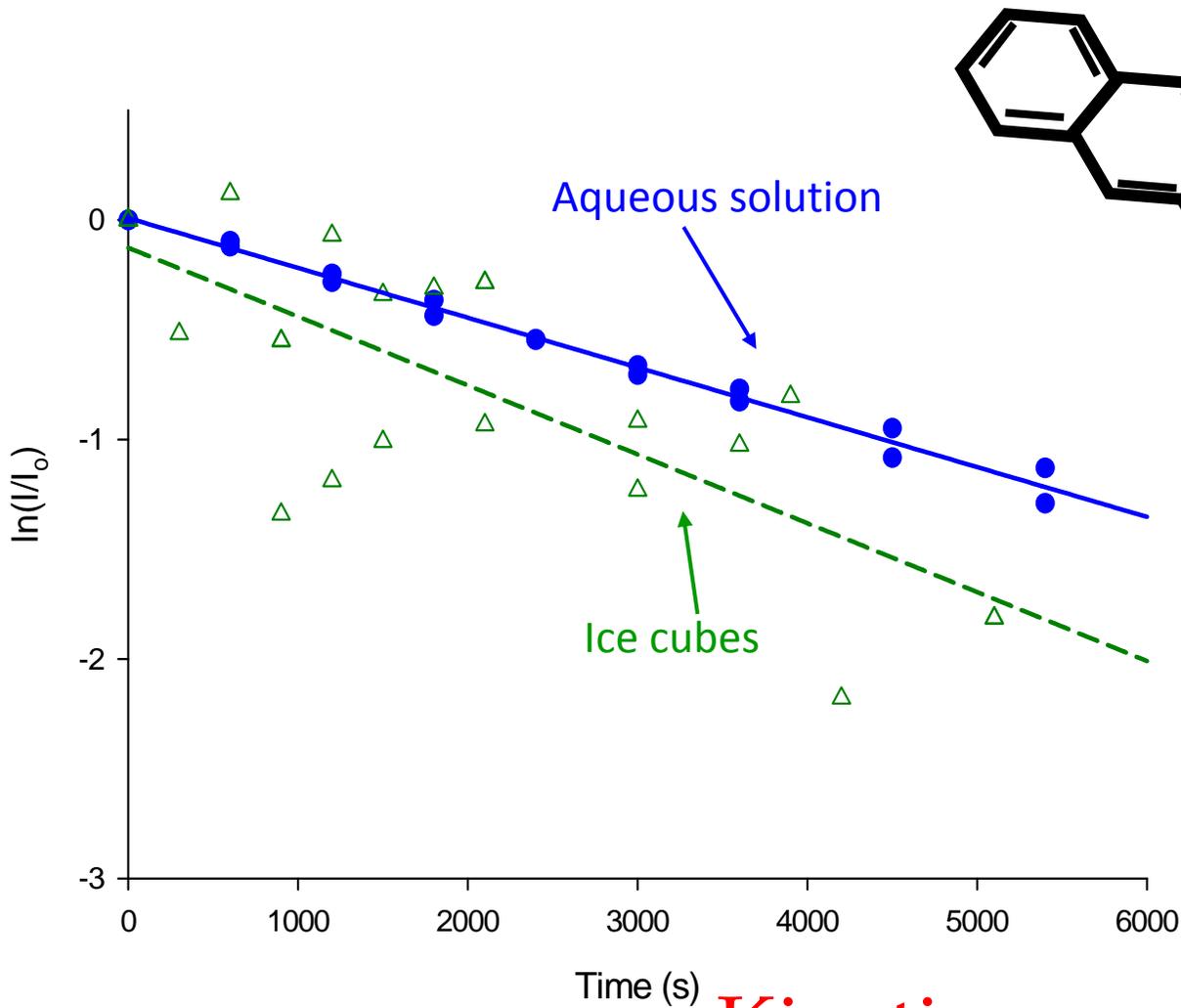
In parallel, laboratory studies of reactions taking place on ice surfaces must be undertaken to obtain adequate rate coefficients. It seems essential that these experiments be performed on ice samples that are prepared from vapor deposition and not the freezing of solution, given our previous discussion on the importance of the mode of formation of ice and of reactant location on reactivity. Additional work to determine the partitioning of species between the ice surface and its volume, not only at equilibrium but as a function of the history of ice crystals,²¹ appears essential.

- How well do we understand “pristine” frozen water as a substrate?
 - Direct photochemistry
 - heterogeneous reactions
 - solute exclusion
 - acid deposition

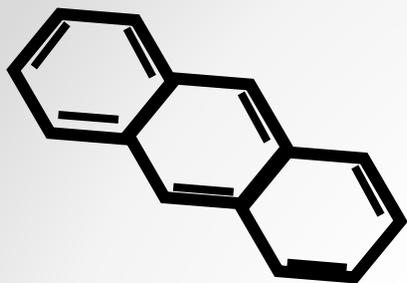
Simple photolysis of aromatic compounds.



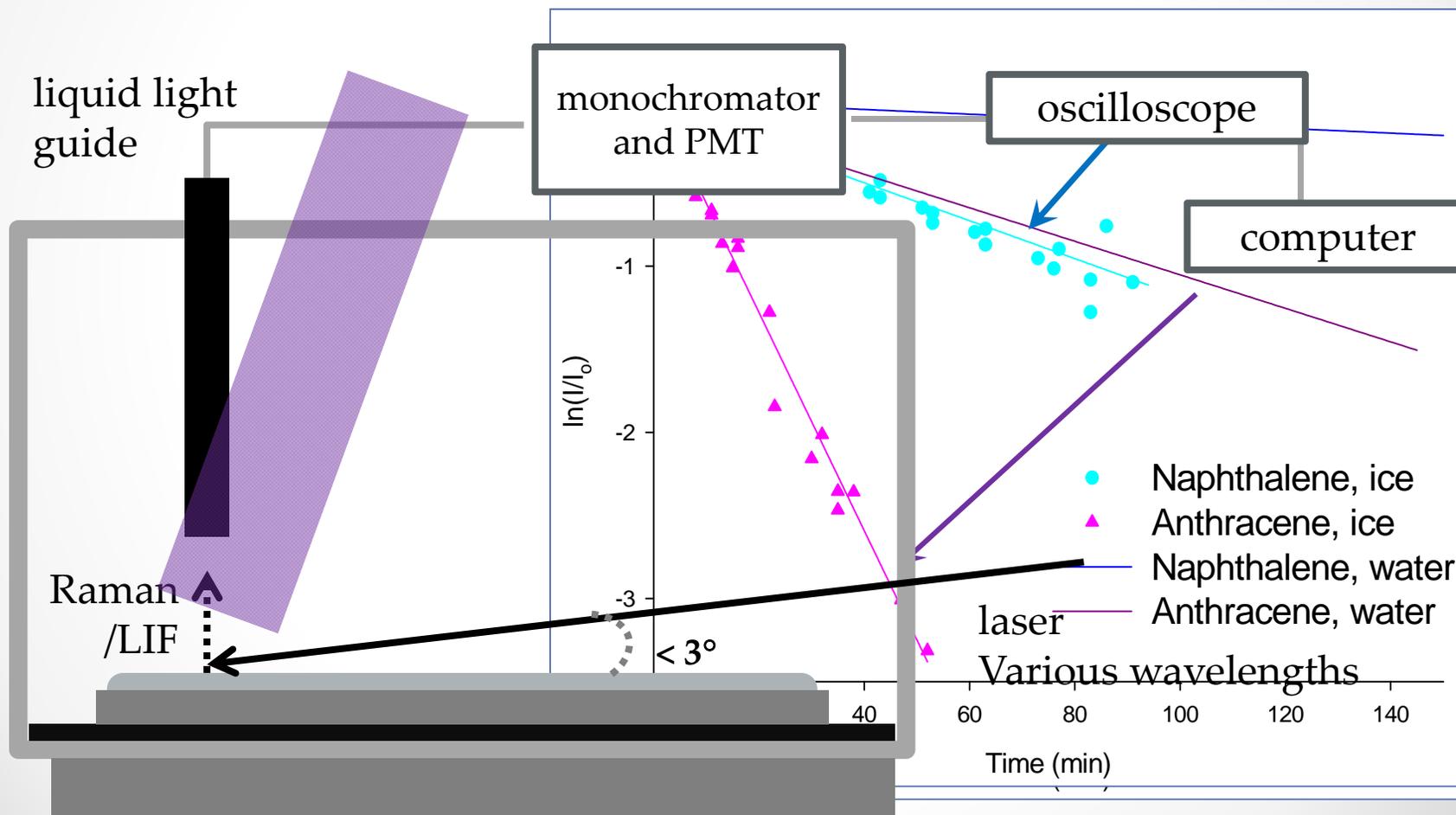
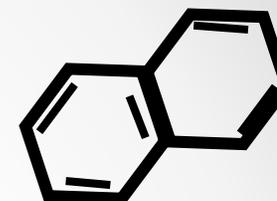
e,



Kinetics are consistent with liquid phase results!



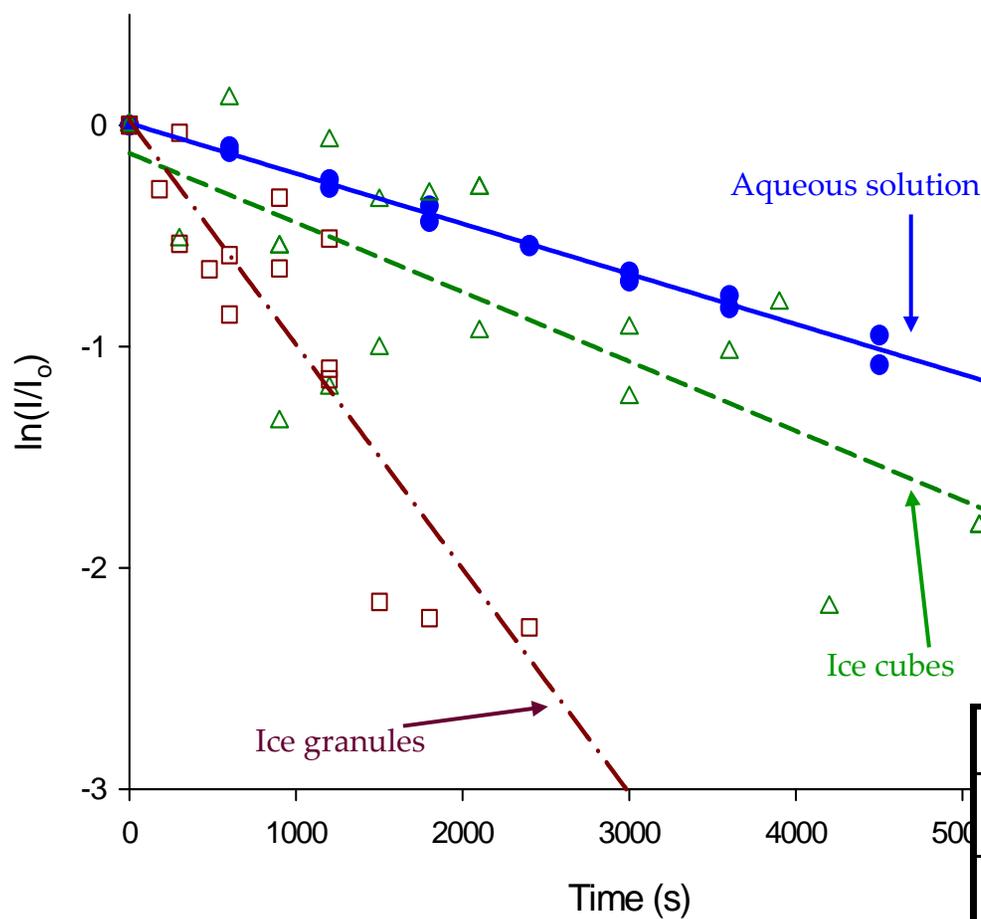
In situ measurements



T.F. Kahan and D. J. Donaldson, *J. Phys. Chem. A* **111**, 1277-1285 (2007)



Anthracene photolysis in bulk samples



Increasing the surface / volume ratio increases the rate!

Medium	$k_{\text{obs}} (10^{-3} \text{ s}^{-1})$
Bulk water	0.25 ± 0.06
Air-water interface	0.17 ± 0.03
Ice cube	0.4 ± 0.2
Ice granule	1.0 ± 0.3
Air-ice interface	1.04 ± 0.08

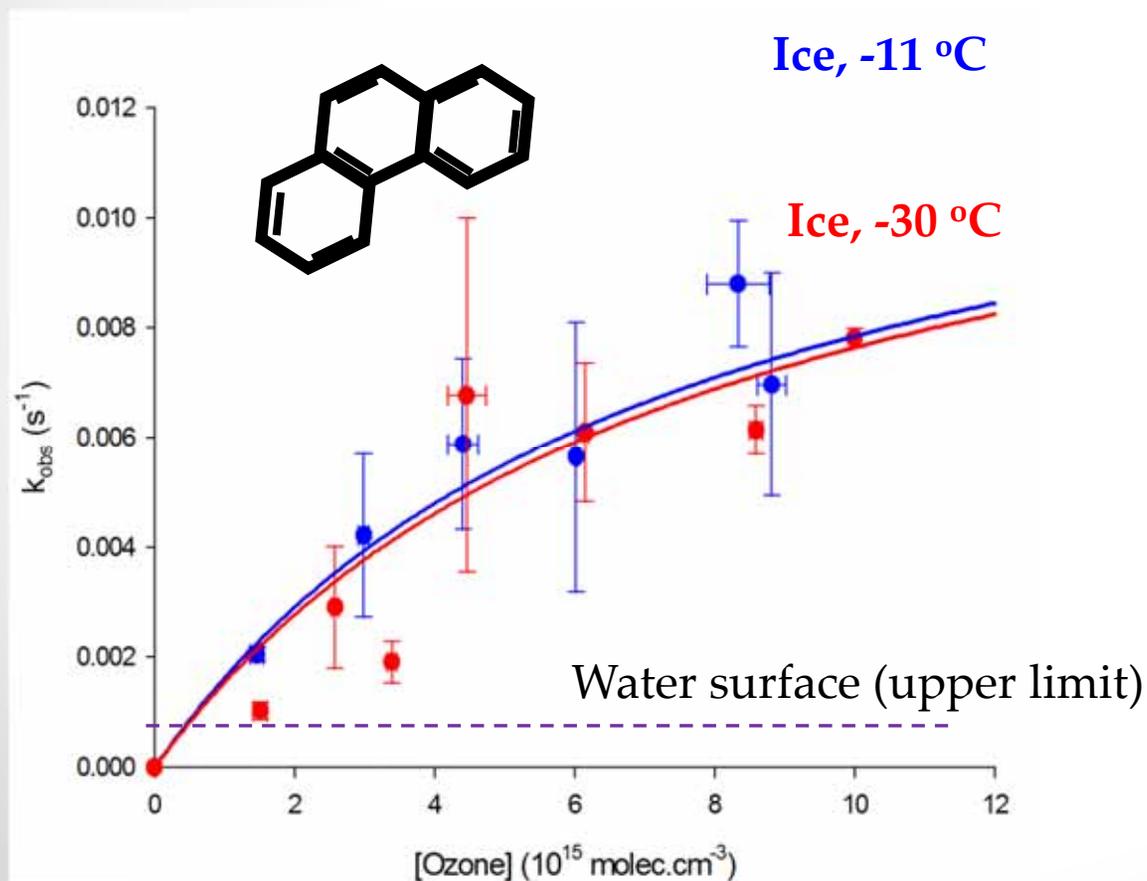
Heterogeneous ozonation:

The loss kinetics of phenanthrene by ozonation at the air-ice interface are (a) faster than in solution; (b) *first order* in phenanthrene

T. F. Kahan and D. J. Donaldson

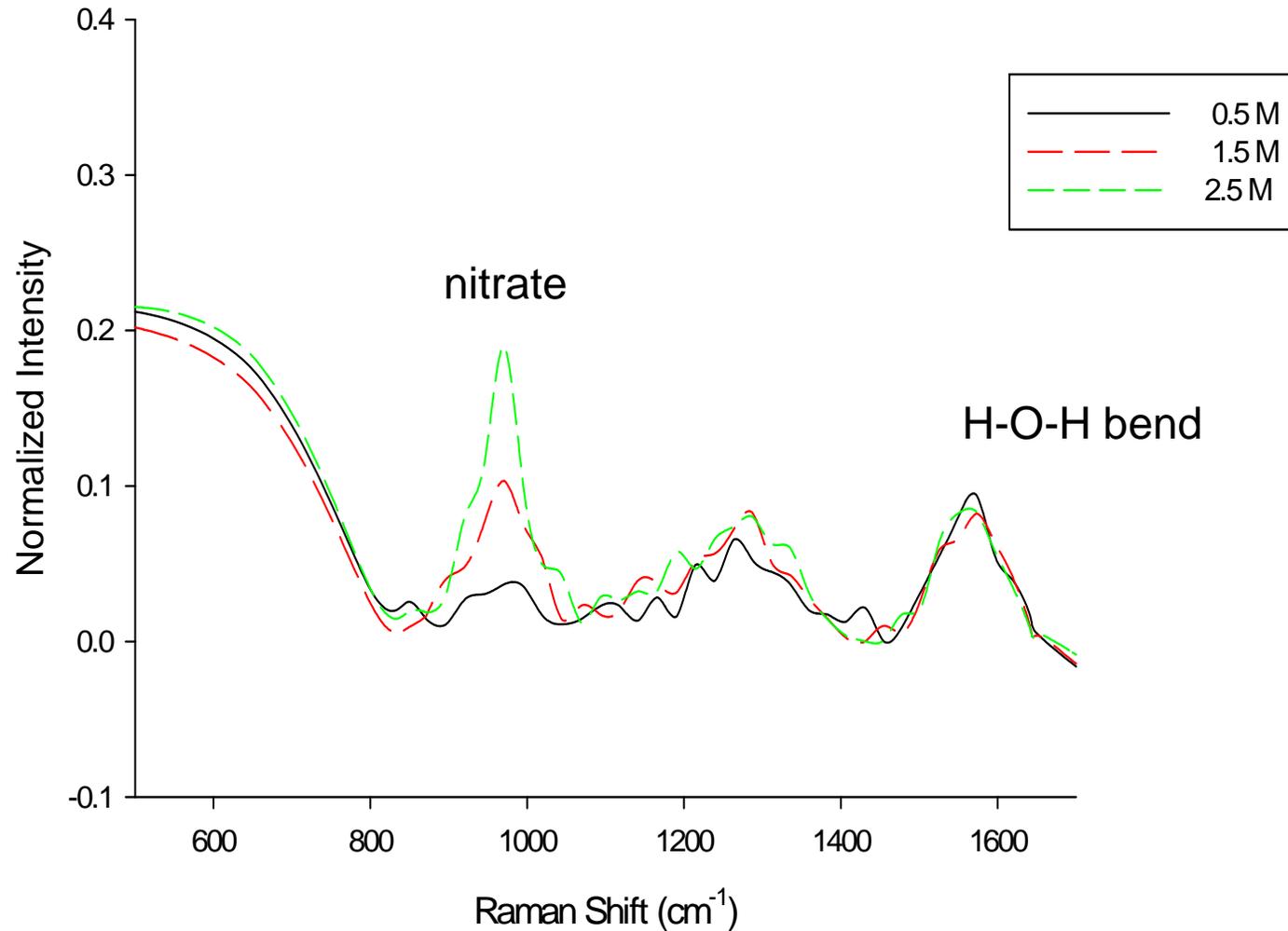
Environ. Res. Lett. **3** 045006

doi: [10.1088/1748-9326/3/4/045006](https://doi.org/10.1088/1748-9326/3/4/045006), (2008)

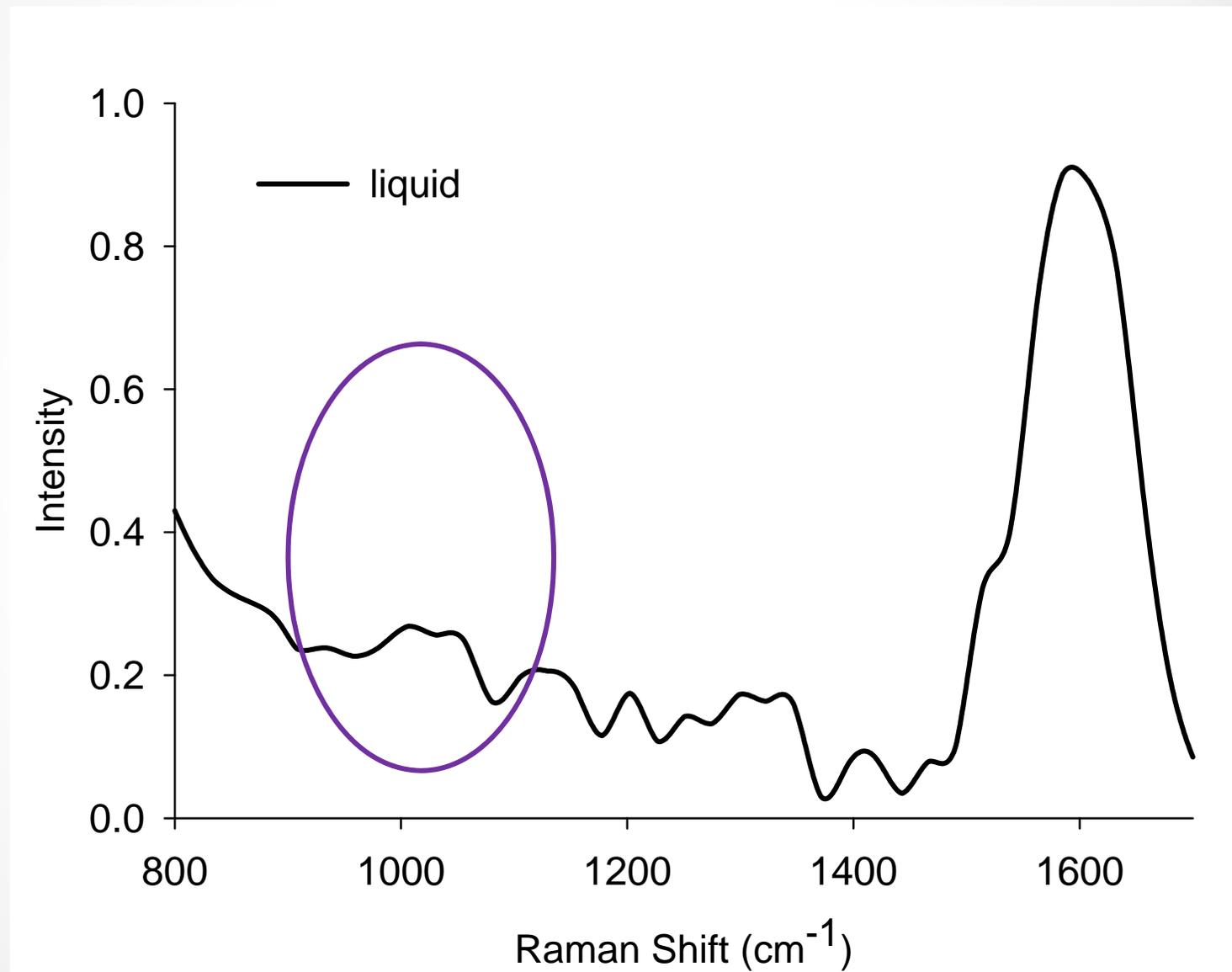


Exclusion 1:

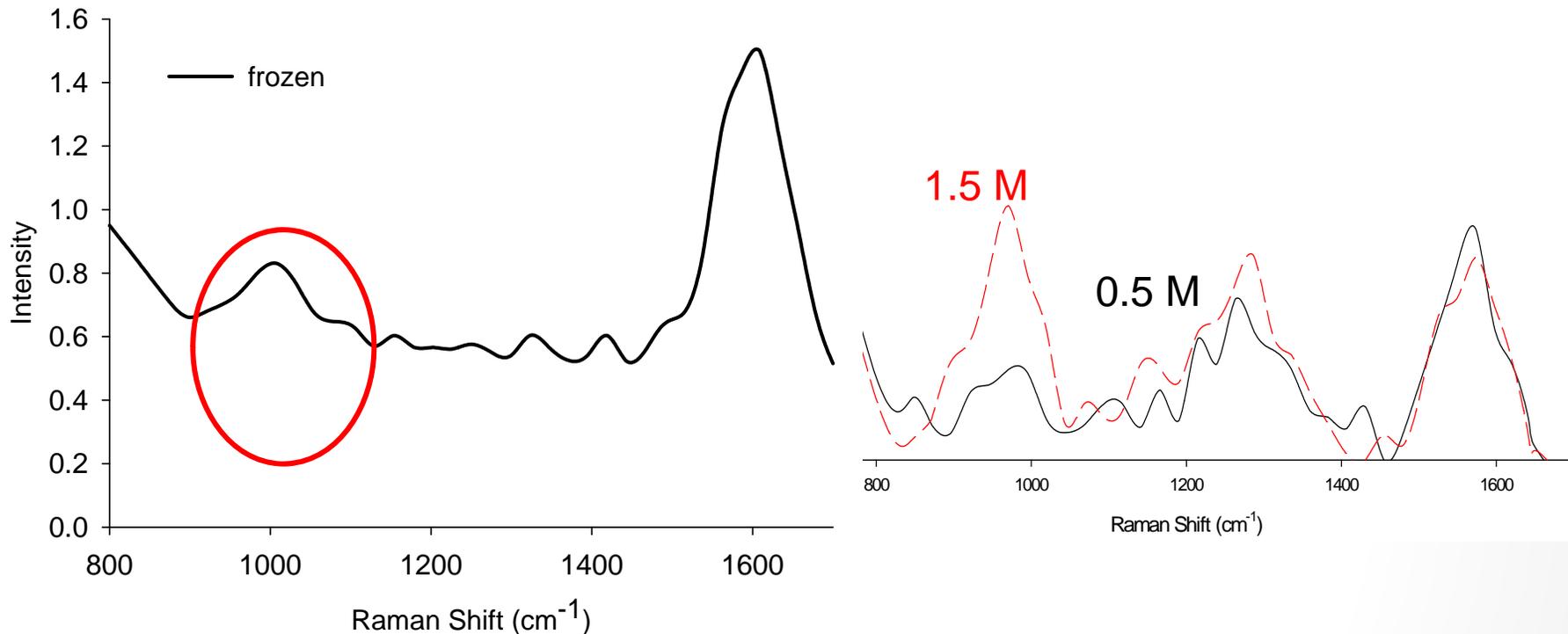
In nitrate-containing solutions, we see nitrate Raman signal at the air-water interface



Frozen 100 mM solutions of $\text{Mg}(\text{NO}_3)_2$



Mg(NO₃)₂·H₂O Phase Diagram



Brine [Mg(NO₃)₂]
19 wt% \cong 1.3 M Mg(NO₃)₂
 \cong 2.6 M NO₃⁻

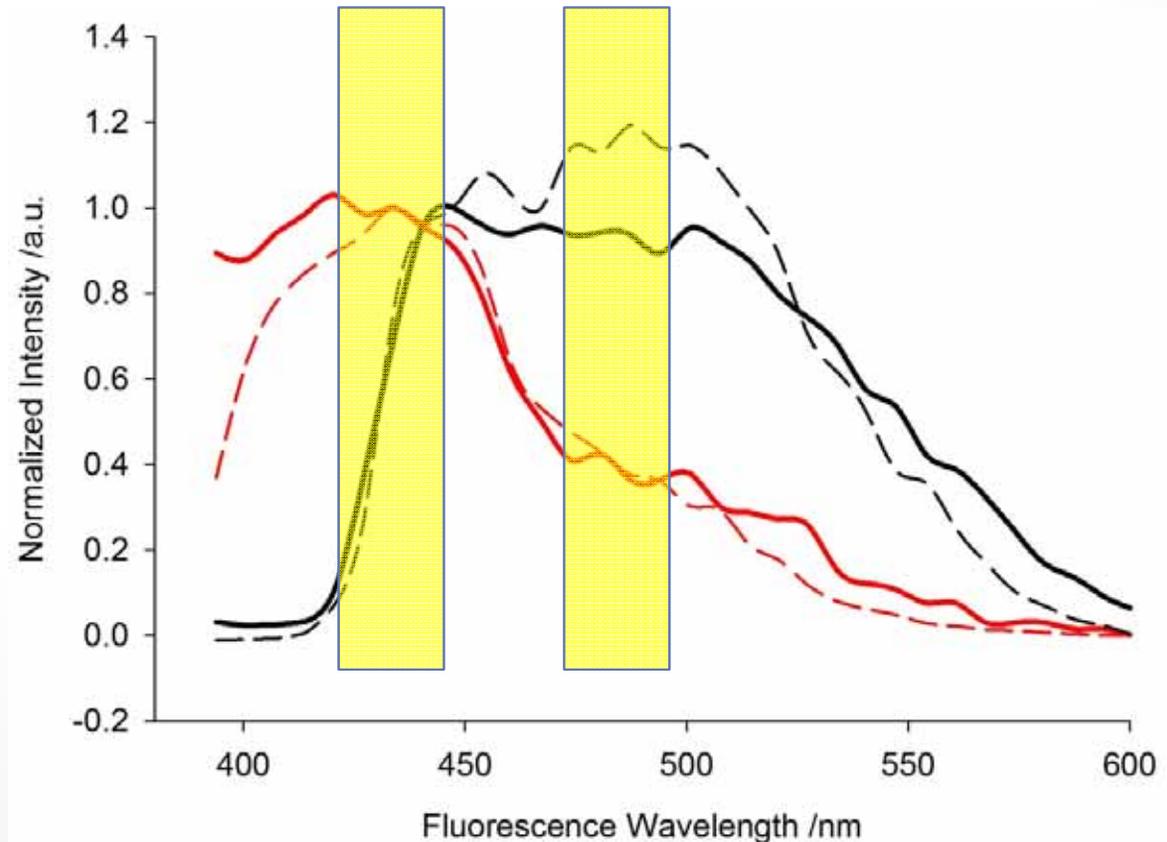
Wren and Donaldson,
J Phys Chem Lett **2011**, 2, 1967

- *Surface [NO₃⁻] not predicted by equilibrium phase diagram*
- *Nitrate must be excluded to liquid pockets or incorporated into ice matrix*

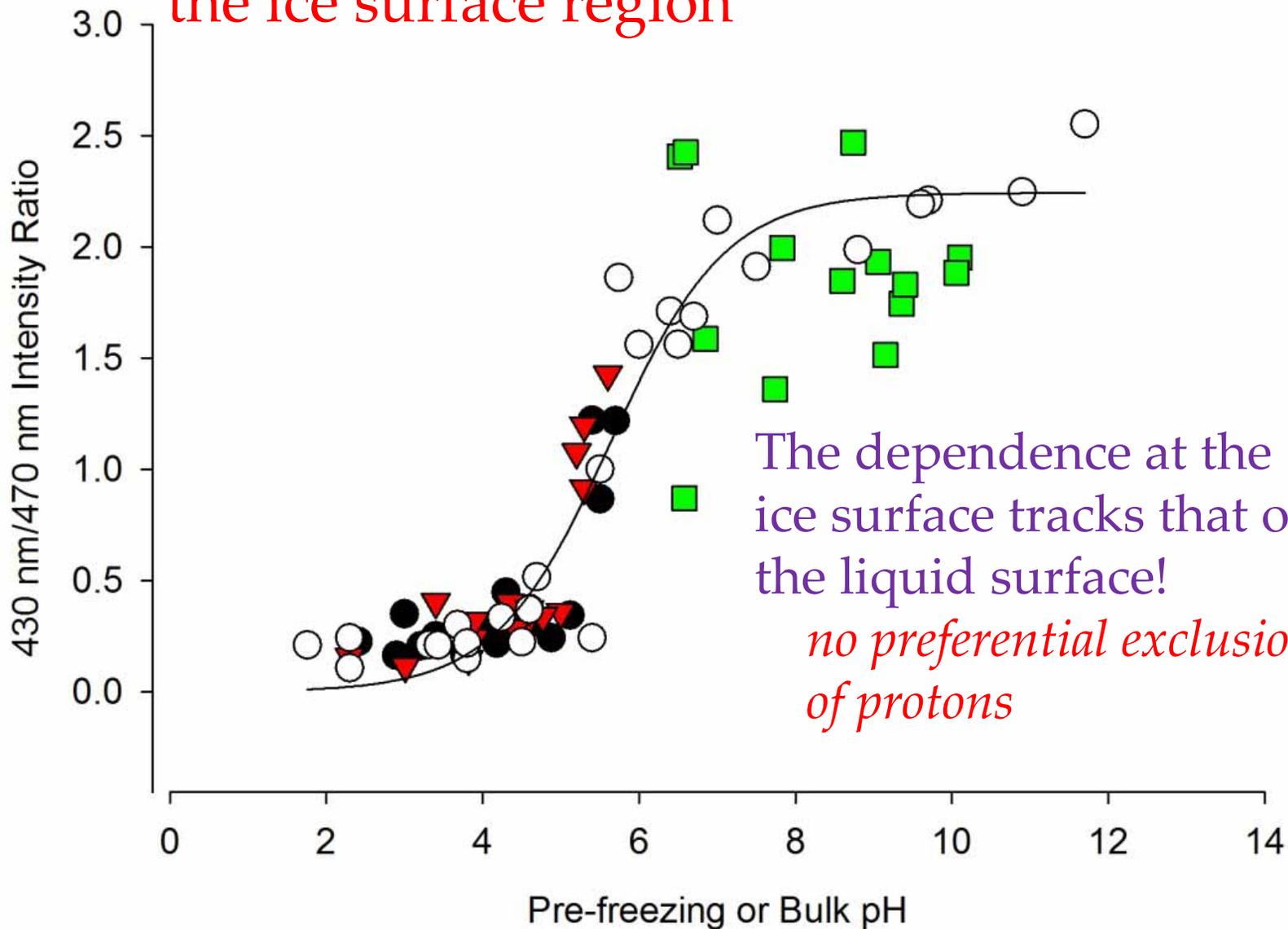
Exclusion 2:

What about proton exclusion? What is the pH in the air-ice interface region?

pH changes are tracked at the frozen surface using a fluorescent dye - acridine



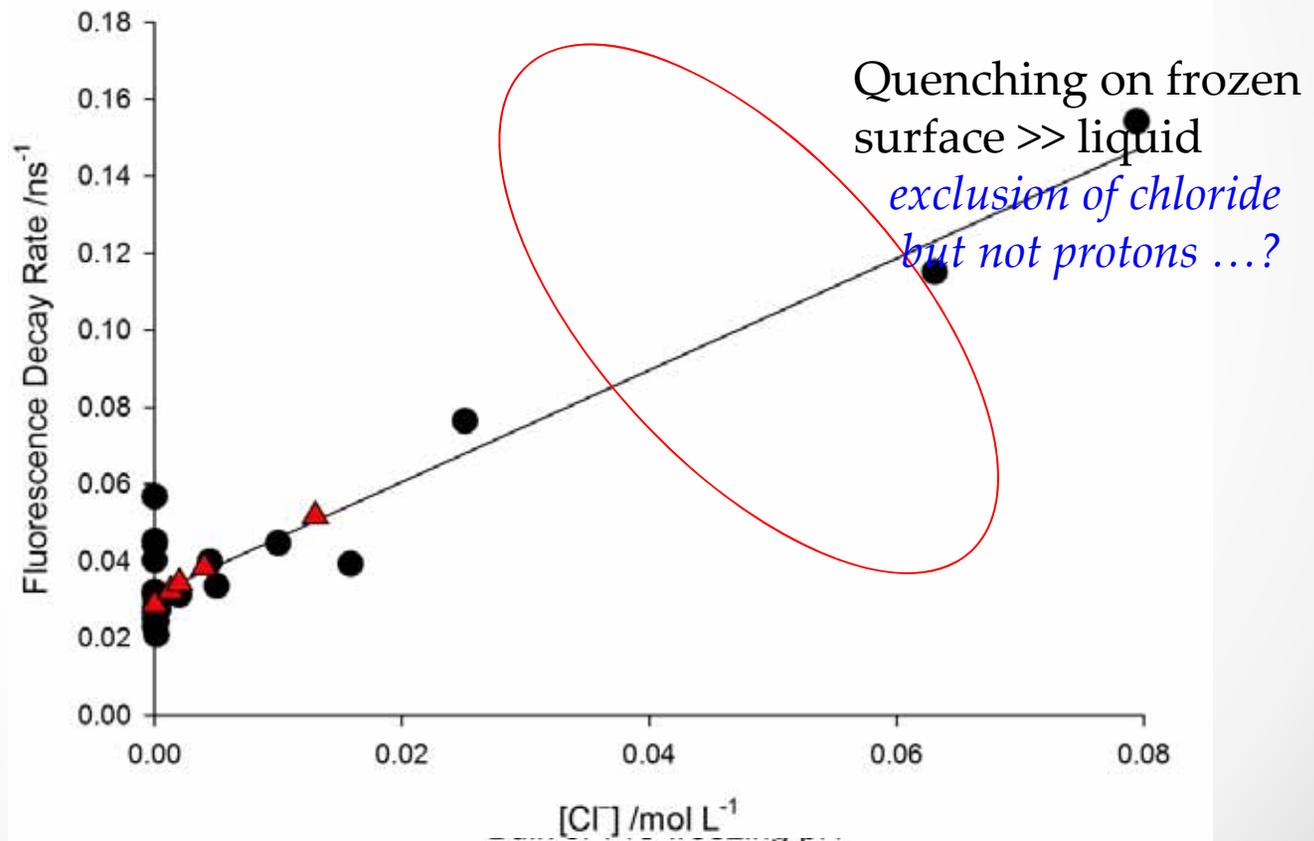
The acridine 430 / 470 nm fluorescence intensity ratio is related to the local pH at the ice surface region



The dependence at the ice surface tracks that of the liquid surface!

no preferential exclusion of protons

Other indicators of ion exclusion: fluorescence quenching of acridine by Cl^-



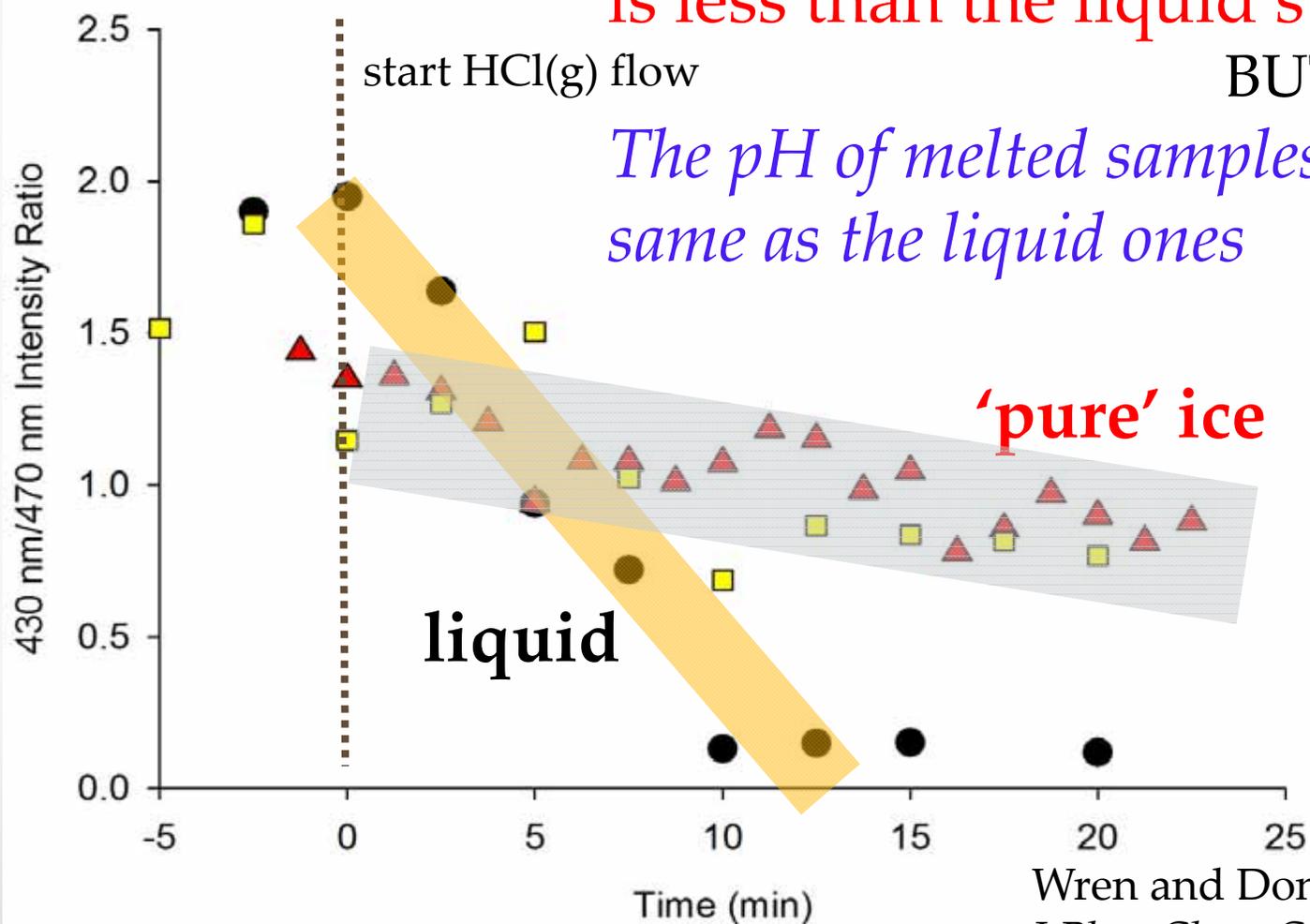
Acid deposition:

Add acid from the gas phase to liquid or frozen ice samples

The pH change at the ice surface is less than the liquid surface!

BUT

The pH of melted samples is the same as the liquid ones



Wren and Donaldson,
J Phys Chem C **2012**, 116, 10171

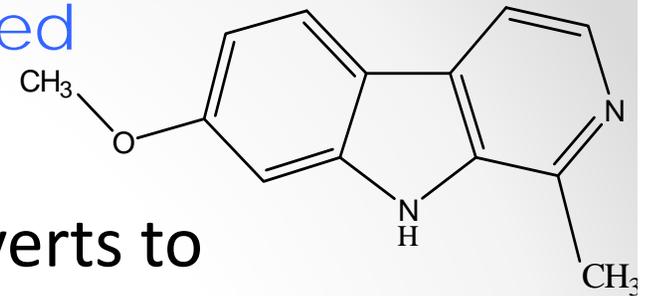
On frozen freshwater solutions ...

- OH region of water Raman spectrum indicates more “ice-like” environment
- Uptake of acids and bases from the gas phase proceeds but the surface pH does NOT track this uptake!
- Kinetics of the heterogeneous ozonation of phenanthrene are much faster than at liquid surface
- Photolysis kinetics within ice matrix well described as liquid-like ... also kinetics on frozen salt solutions. *BUT at frozen freshwater surface, kinetics are much faster.*

- How about frozen salty water?
 - Direct photochemistry
 - heterogeneous reactions
 - acid deposition
 - sea ice chemistry

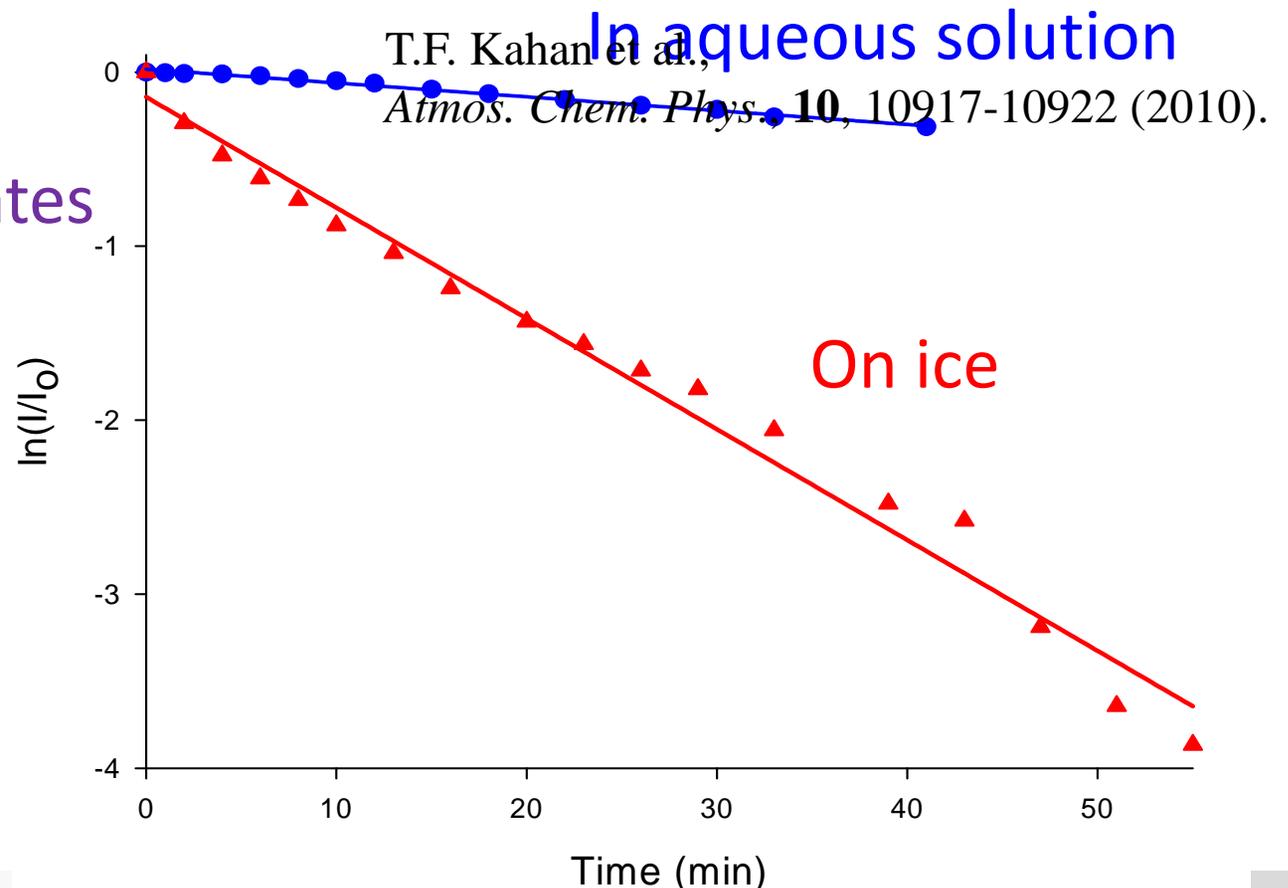
Simple photolysis:

A photolysis rate enhancement is observed for harmine on the ice surface as well.



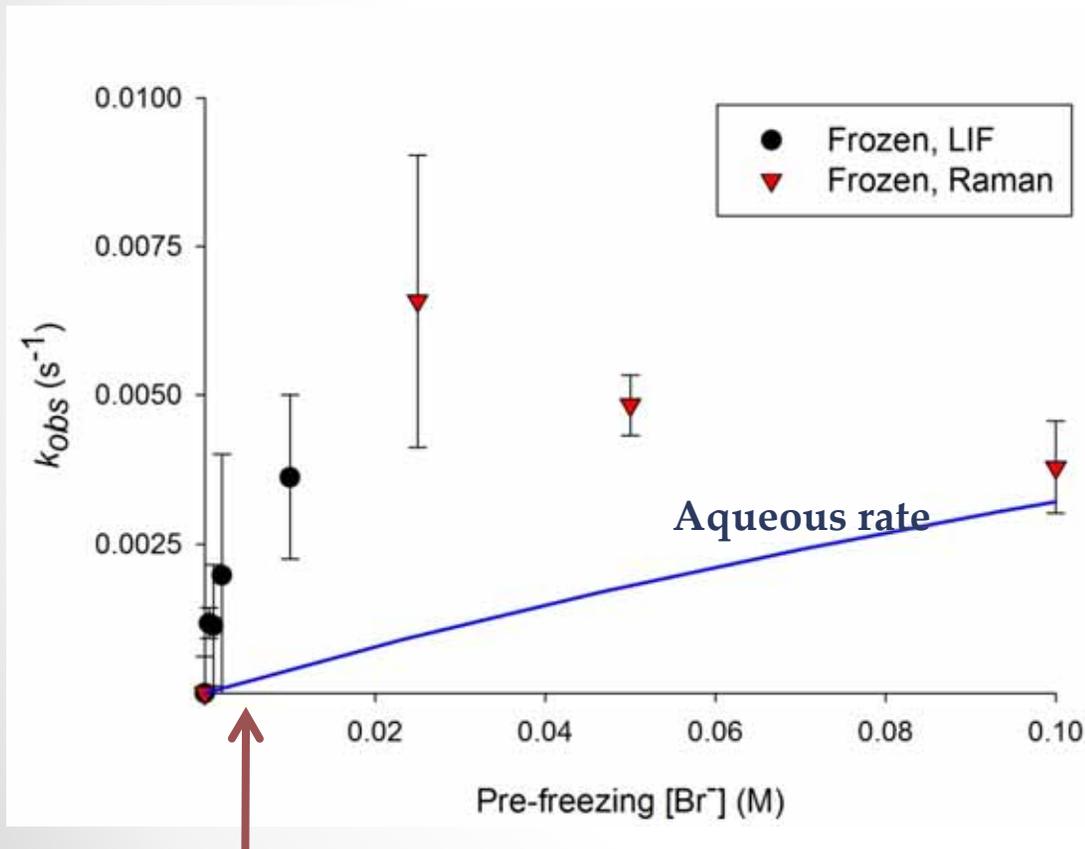
But on frozen salt solutions the rate reverts to that seen on the water surface

Exclusion of salts during freezing creates an aqueous brine layer at the surface



Heterogeneous ozonation:

On salty water the ozonation of halides takes place faster than at the surface of the corresponding liquid.



Sea water [Br⁻]

- *Reaction proceeds more quickly on ice surface* than aqueous surface for same bulk (pre-freezing) halide concentrations
- Accelerated rates probably due to halide exclusion

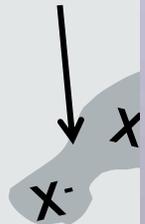
S. N. Wren et al.,
J. Geophys. Res. **115** Article Number: D16309 (2010).

The much faster reaction rates on ice are best understood as a consequence of salt exclusion during freezing, yielding highly concentrated brines on the surface

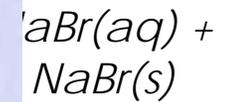
Ion Exc

X^-
brine

brine in
pocket



Appar
the br

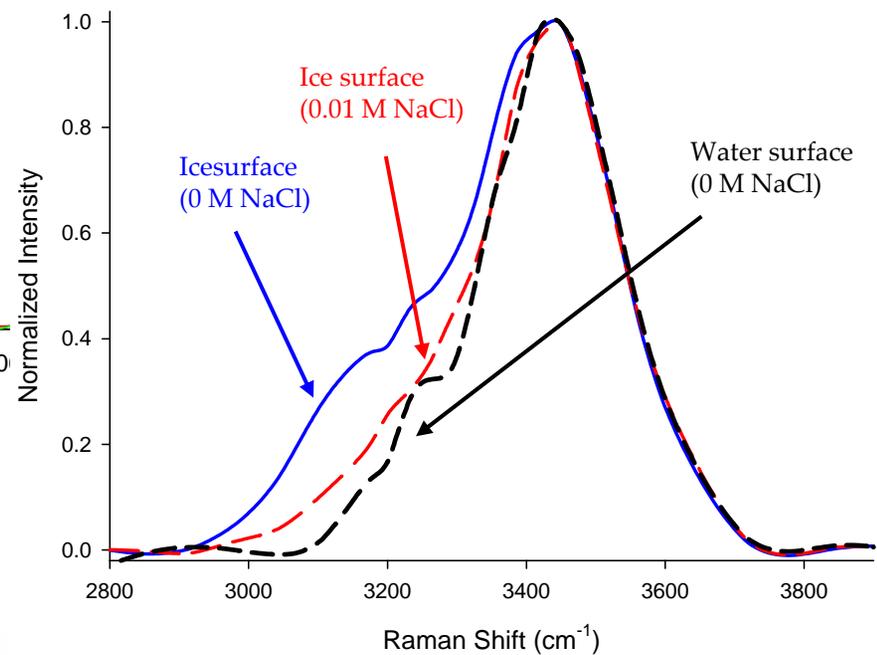
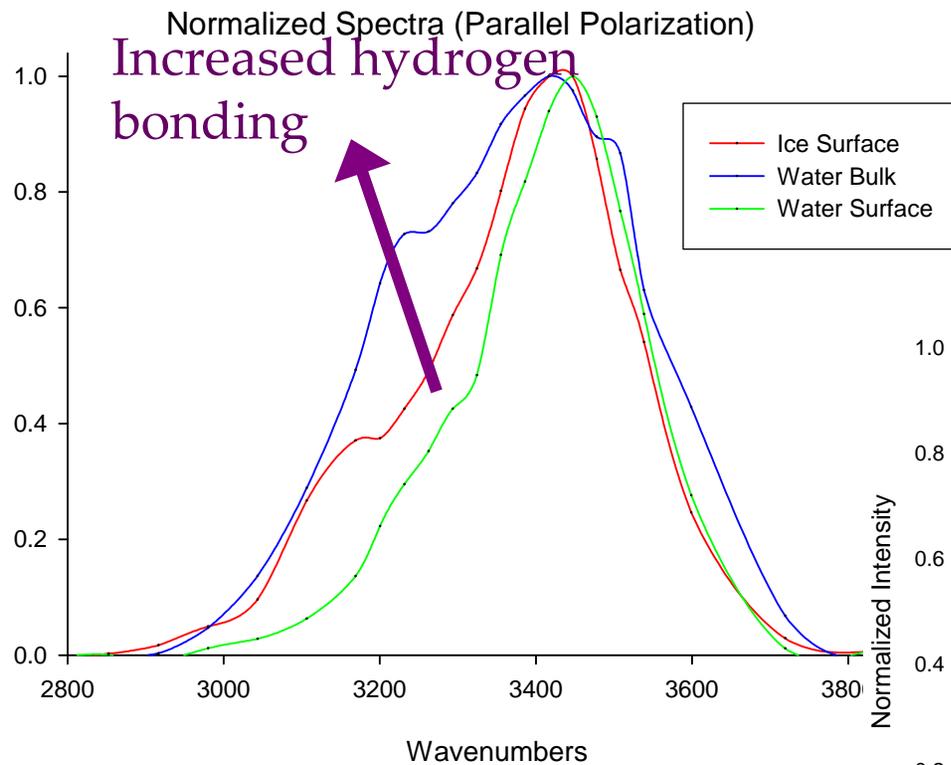


temperature

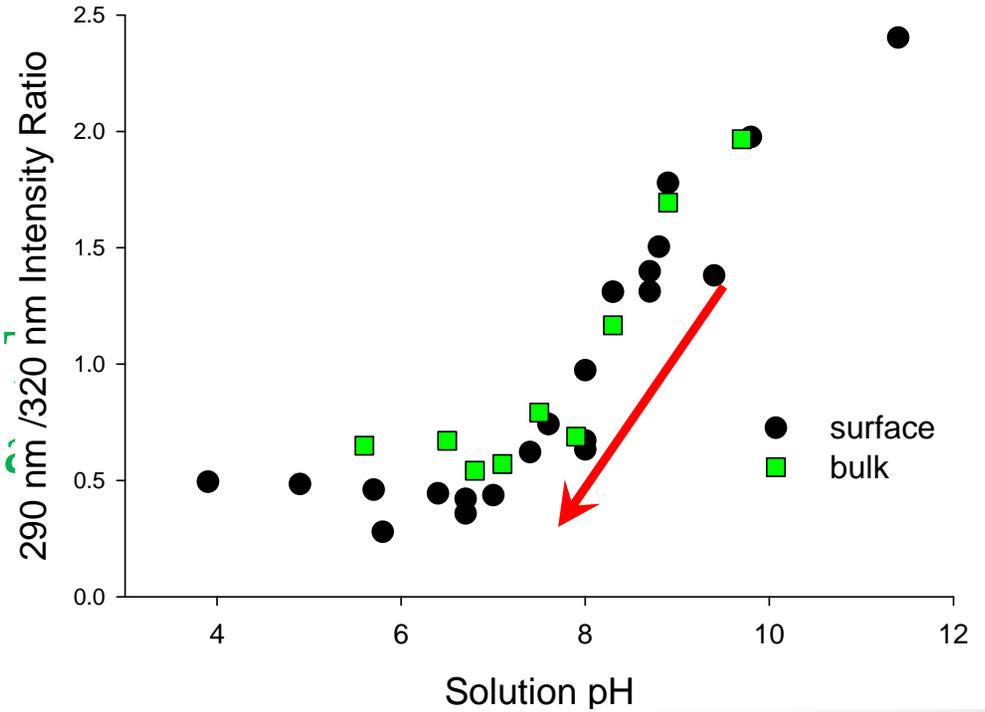
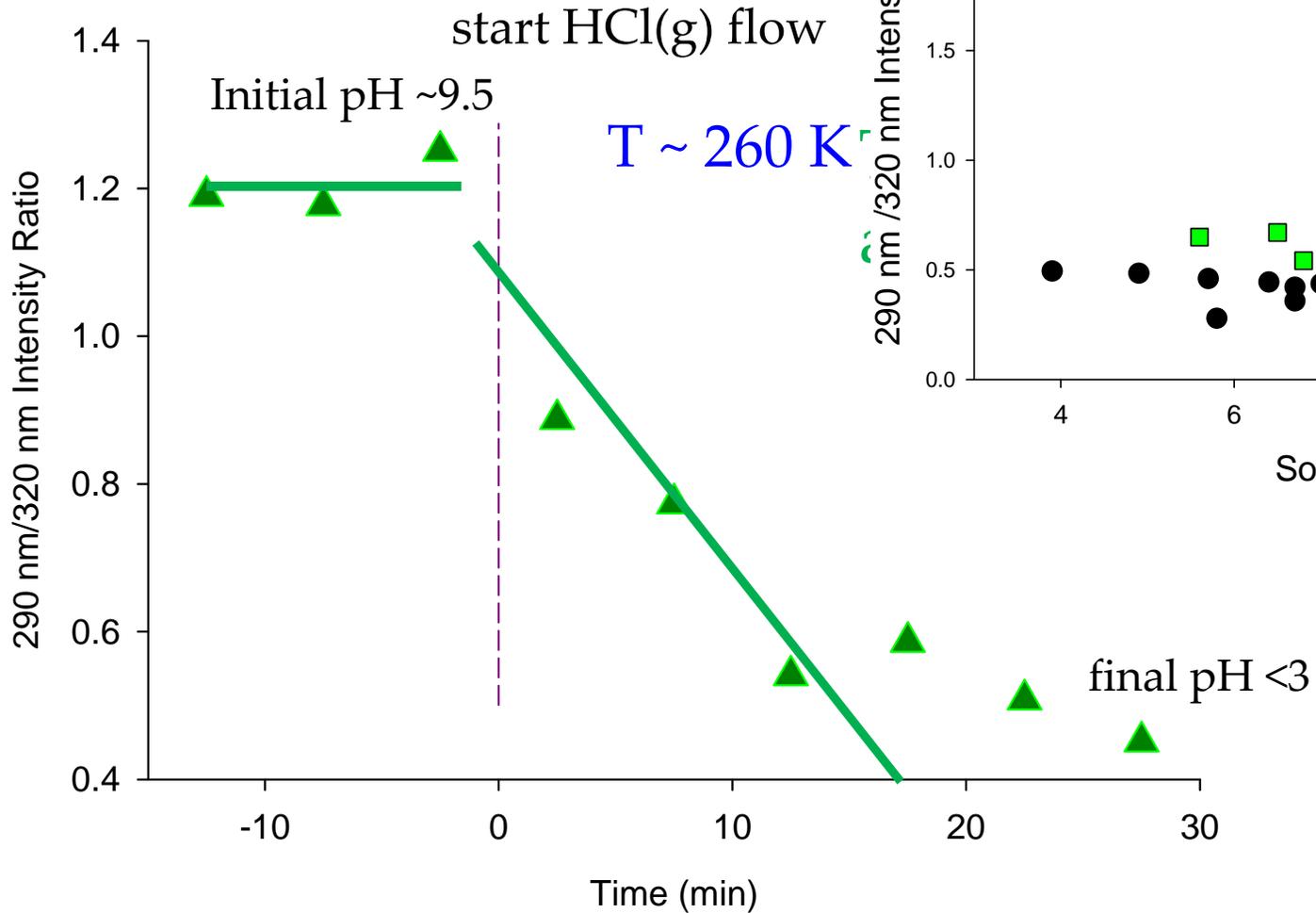


the $[X^-]$ in

Raman spectra of OH stretch at frozen salt water surfaces are consistent with exclusion of salts

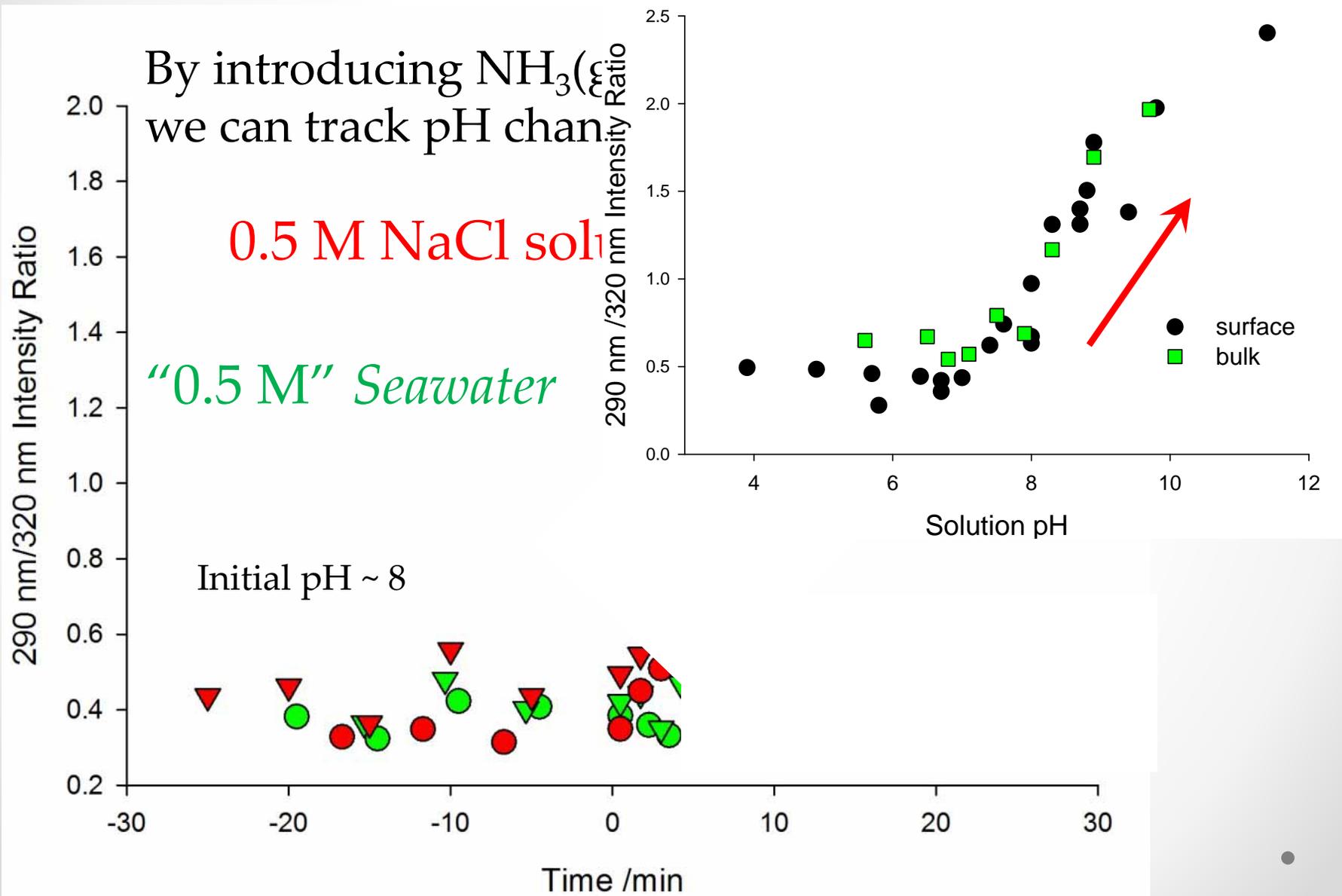


We acidify frozen salt water from the gas phase



Is the surface of frozen seawater buffered?

liquid seawater is buffered by CO_2 and HCO_3^- (pH ~ 8.2)



So on frozen salt solutions ...

- OH region of water Raman spectrum indicates “liquid-like” environment
- Uptake of acids and bases from the gas phase proceeds as though to a liquid surface
 - Interesting and important result that sea-ice surface maintains buffering capacity!
- Kinetics of the heterogeneous ozonation of bromide well described as occurring in liquid/at liquid surface
- Photolysis rates can be tuned from “ice surface” to “liquid surface” by inducing a brine layer

- Snow or ice?

- Hardly any laboratory experiments on true snow

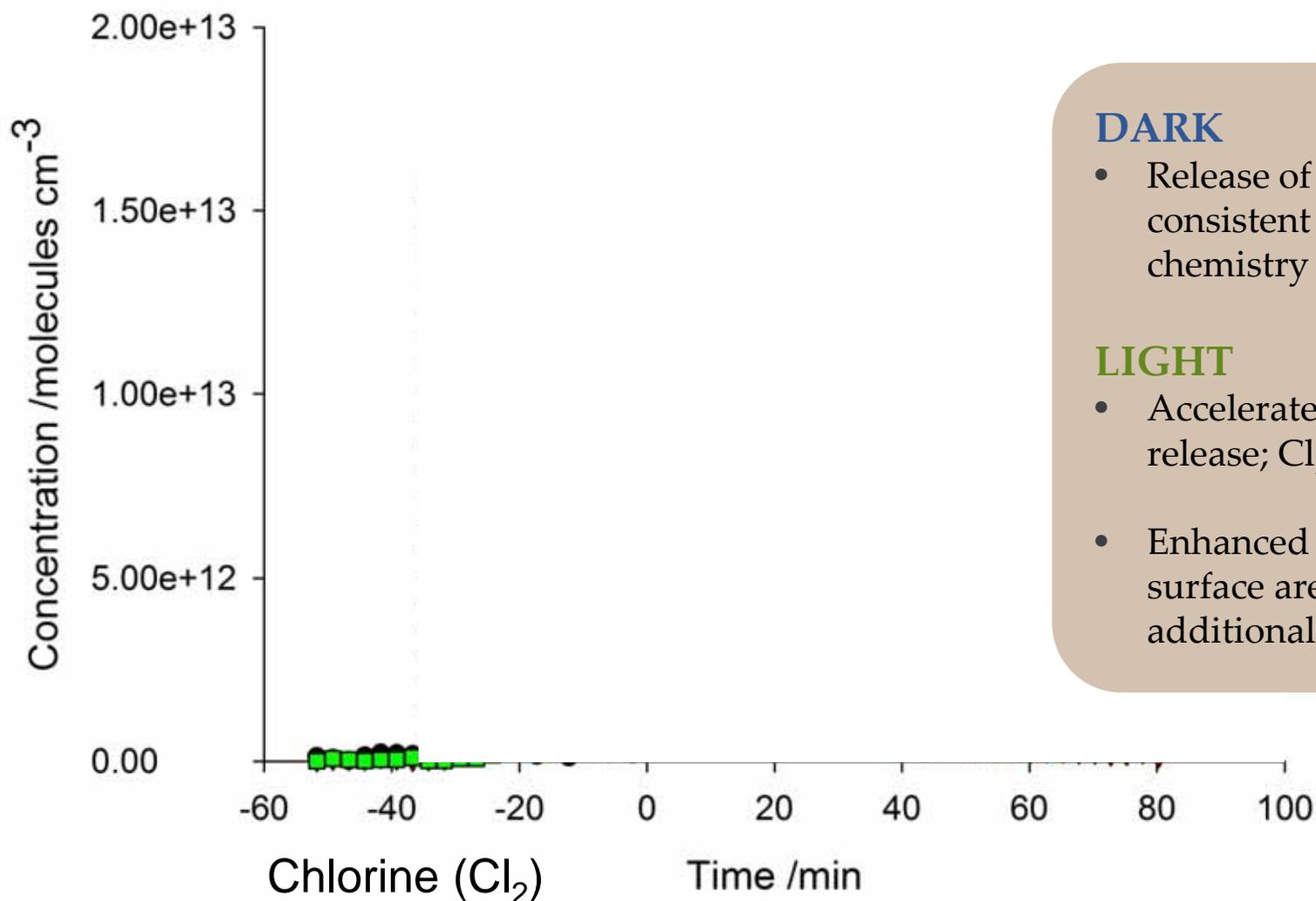
Chlorine release from illuminated, ozone-ventilated salty "snow"

Wren et al. ACPD 2013



Typical Experiment: BASE scenario

$[\text{O}_3](\text{g}) = 1 \times 10^{15} \text{ molecules cm}^{-3}$



DARK

- Release of Br_2 and BrCl , consistent with known chemistry

LIGHT

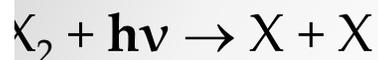
- Accelerated Br_2 and BrCl release; Cl_2 production!
- Enhanced by acidity, surface area and additional $\text{Br}_2(\text{g})$

- Bromine Chloride (BrCl)

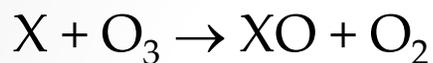
Finlayson-Pitts, 2003; Oum et al., 1998; Wren et al., 2010; Oldridge and Abbatt, 2010

Snowpack halogen explosion

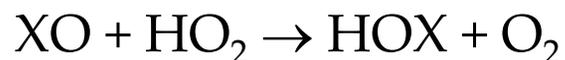
'seed' bromine



light



ozone depletion



HO_x source?



surface area



acidity



>> organic contaminants
(HO_x precursors)

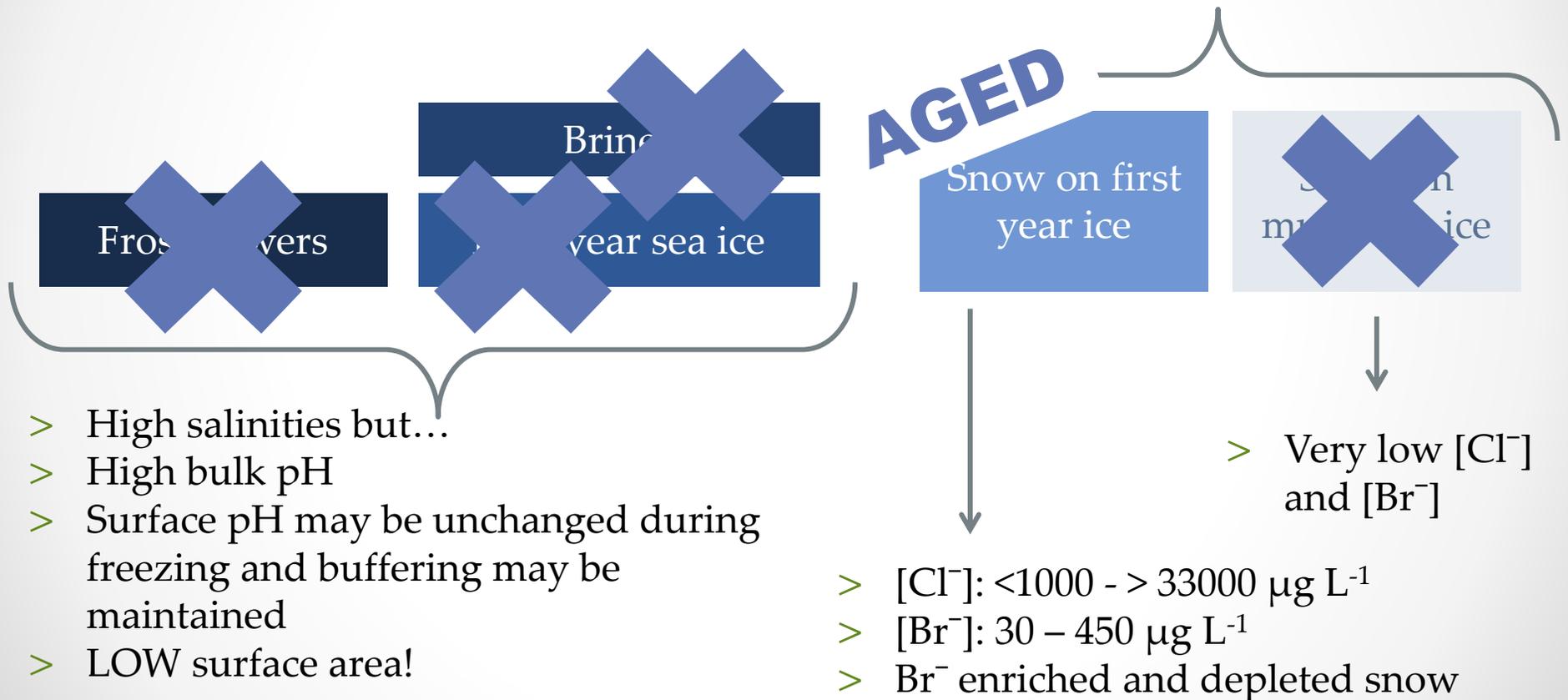
>> natural snows release
VOCs, HCHO and HO_x
directly^{1, 2}

Fan and Jacob, 1992; Simpson et al., 2007
Adams et al., 2002; Huff and Abbatt, 2002;
Huff and Abbatt, 2000; ¹Gao et al., 2013;
²Domine and Shepson, 2002

OASIS Implications

Where is chlorine activation going to occur?

- > High surface area
- > Lower pH



Unanswered questions

- Why is the reactivity at the “pure ice” surface (QLL??) different?
- What is going on with protons at this interface?
- How important is it to deal with “snow” vs. “ice” in the lab?
 - What is the role of snow morphology, metamorphosis? Does it ultimately matter exactly where chemistry takes place?
- Do we need to build an OASIS mesocosm experiment?