Snow Photochemistry:
1. Light Absorption
2. Oxidant Generation
3. Impacts on Halogens and Organics

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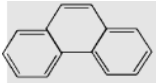# But First – A Discussion of Liquid-Like Regions

- Florent and Jamie and co-authors say "Non!"

- But I say "Oui!" or at least "Généralement"
  - Are laboratory ices the same as snow? No.
  - Are laboratory ices a good mimic for snow? Probably…

- Semantics: what is cut-off between a QLL (no, or very low, solutes) and a QBL (quasi-brine layer with higher solute concentration)?
  - Use "liquid-like regions" (LLRs) as more general term
  - LLRs: solutes are not just at air-ice interface; QLL might be special case
  - There are other ice reservoirs: bulk ice, insoluble particles, more?

- We typically make our ice by slowly freezing aqueous solutions
  - Samples are illuminated, melted, analyzed
  - Thus we are measuring the entire sample
  - Based on our experimental evidence, we believe solutes are present in LLRs, although we do not know their locations (inclusions, interface…)
 - Measure photon flux using 2NB in same pellet size/geometry/container

Oui #1: Direct h𝑣 in/on Ice Behaves Like Liquid

- OH production from illumination of NO_3^-, NO_2^-, or HOOH (< 200 µM)
  - Ice results match T-dep of solution
  - Ice photolysis behaves like supercooled solution
  - Oui #2: Using lab NO_3^- quantum yields (QYs) predicts NO_x fluxes similar to field measurements
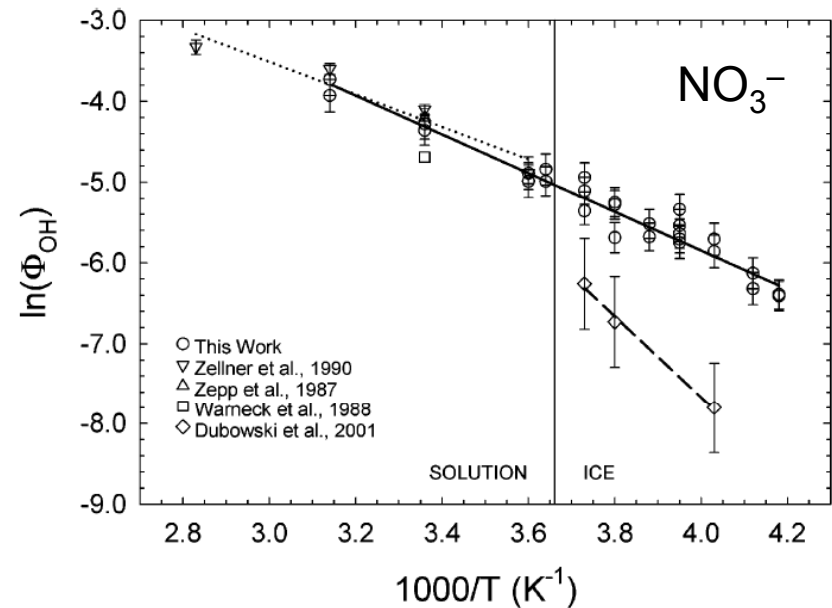
- PAH photodegradation
  - PHE = phenanthrene
  - 0.8 µM in Milli-Q or melted Summit snow; refroze as 1-mL pellets
  - Put on snow at Summit (Aug, midday)
  - Decay same in snow and Milli-Q
  - QY comparable to supercooled water
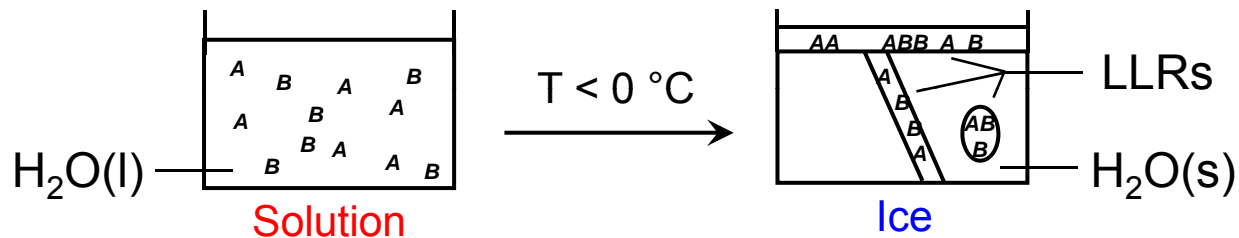 - Gives short lifetime (hrs): Summit PAHs probably not in ice but in PM
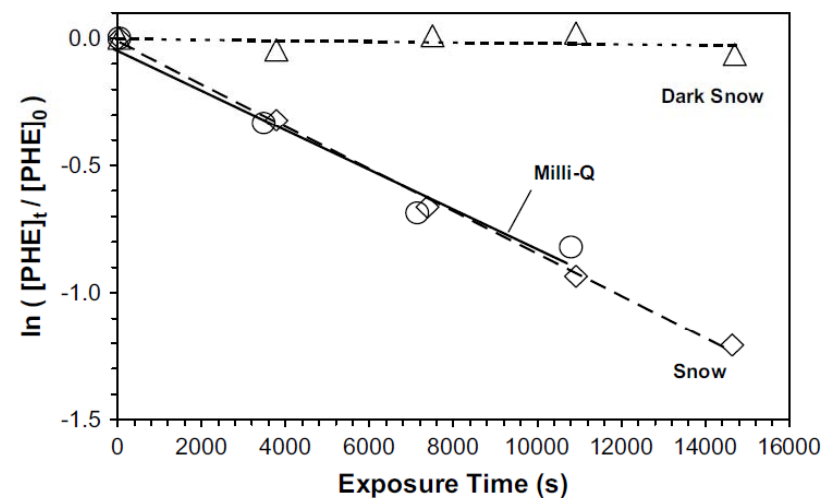
What about 2nd-Order Reactions?
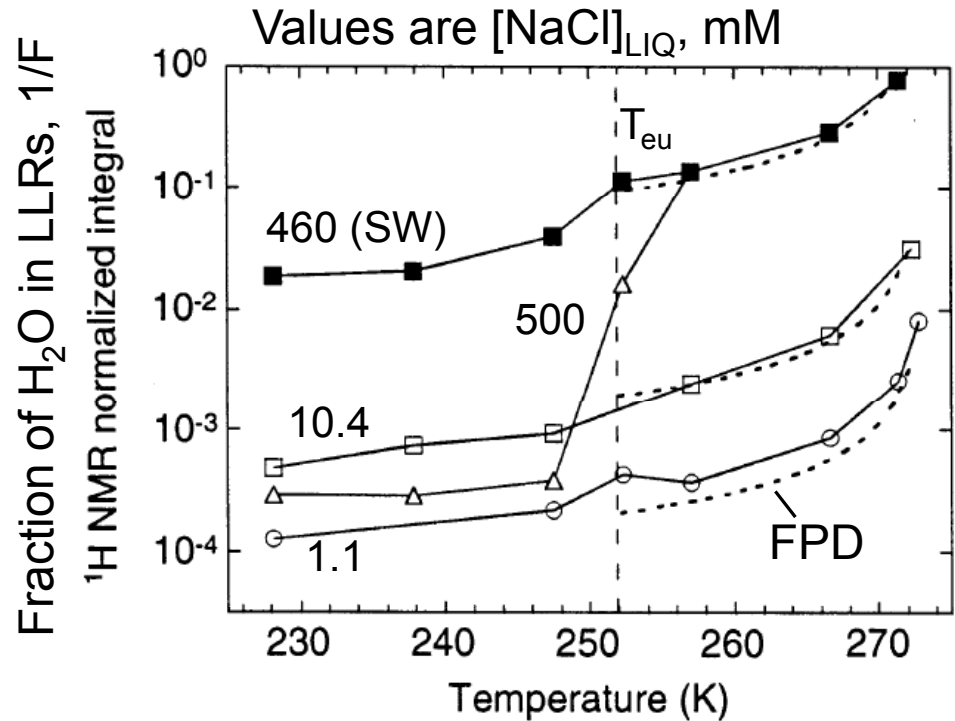## First, Consider a Freezing-Point Depression (FPD) Model of LLRs

- FPD picture for freezing a solution: solutes (A and B) are excluded from ice matrix and segregated into liquid-like regions…

- FPD model prediction of freeze-concentration factor, F (= Φ^{-1})

- F = [A]$_{LLR}$ / [A]$_{LIQ}$ if all A ends up in LLRs and does not precipitate
  $1/F$ = Φ = V_{LLRs} / V_{LIQ}, i.e., fraction of H$_2$O(liq) that end up in LLRs

- Dependence of F in FPD model
  - [TS] in LLR is set by T, independent of salt (e.g., [TS]$_{LLR}$ = 5.3 M at –10 °C)
  - Thus F increases with lower total solute concentrations in solution
  - Similarly, F increases with decreasing T (which increases [TS]$_{LLR}$)

Oui #3: Past Lab Evidence for FPD Model

- **Composition measurements**
  - Cho et al. (2002) used ^1H NMR to quantify fraction of H_2O present in LLRs in frozen NaCl ices
  - $F = (^1H$ NMR integral$)^{-1}$
  - Above T_{eu}, msmts fit FPD model fairly well: $F \sim 10\text{-}3000$ near T_{eu}
 - Below T_{eu} still evidence for LLRs

Values are $[NaCl]_{LIQ}$, mM

Fraction of H_2O in LLRs, $1/F$

^1H NMR normalized integral

460 (SW)

500

10.4

1.1

T_{eu}

FPD

Temperature (K)

Cho et al., JPC A, 2002

- **Past photochemistry measurements**
  - Grannas et al. (2007) measured photochemistry of 2nd-order actinometer in ice
  - Msmts comparable to FPD for F up to ~ 70; underestimate F w/other conditions

Oui #4: $^1O_2^*$ to Measure Freeze-Concentration Factors

- Method
  - Make solution with sensitizer (Rose Bengal), $^1O_2^*$ probe (FFA), salt to adjust total solute (TS) concentration
  - Illuminate (549 nm); monitor FFA loss
  - Study as solution and ice pellets
  - Normalize results to photon fluxes
  - $F \approx$ ice rate / solution rate

- Results
  - Initial work (top): good agreement for $T > T_{eu}$ and TS > 1 mM
  - Current work (bottom): good agreement for TS as low as 30 μM
  - Difference: lower [RB] in new work
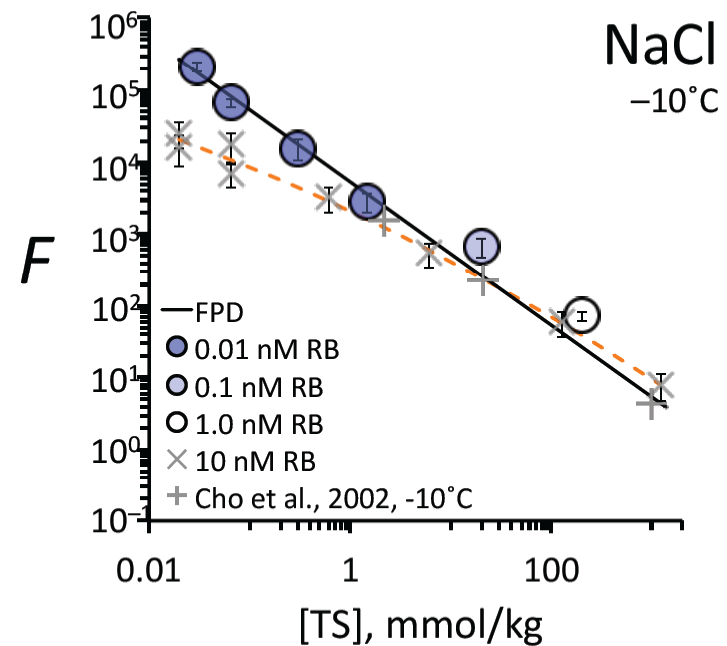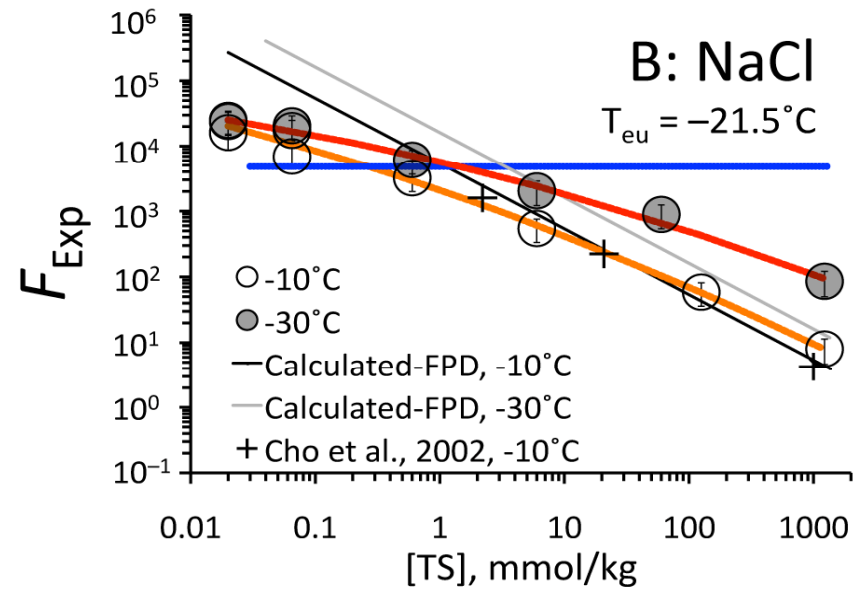
Liquid-Like Regions "Conclusions"

- Are laboratory ices - and FPD - a good model for snow?
  - Probably in many (most?) cases
  - But for solutes that…
    - Precipitate, evaporate, aggregate, etc.
    - Need to also consider these processes
  - Even with LLR ≈ solution, situation is complicated and depends on [TS] & T

- Jamie & Tara's results show chem at "clean" air-ice interface is different
  - Probably important for volatile solutes that partition to interface
  - Might be important more broadly

- Much more work to do
  - Use field observations to help support/rebut laboratory results
  - Need lab studies of solute locations in different ice reservoirs (bulk ice/LLR/QLL/PM) and their chemical differences
  - Framework for including LLR/QLL/etc. chemistry: end of talk

- Discussion of LLR/QLL/etc. before I move on to next topic?

And now, my real (abbreviated) talk…

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Introduction

- Oxidants likely drive much of snowgrain chemistry, e.g.,
    - OH (hydroxyl radical) is important for oxidation of Br- and organics
    - $^1O_2^*$ (singlet oxygen) probably important oxidant for some organics
    - $^3C^*$ (excited triplet states) might also be significant sink for organics

- First step in oxidant formation is typically light absorption by a chromophore
    - e.g., OH formed by photolysis of HOOH, NO_2^-, and NO_3^- on snowgrains

Light Absorption by OSIS at Barrow

- Light absorption by filtered, melted terrestrial snow (left figure)
  - HOOH, NO_3^-, and NO_2^- have insignificant absorption (but impt for OH formation)
  - HULIS (humics/fulvics?) account for ~ 50%; Unknown species ~ 50%

- Light absorption by filtered, melted, frost flowers, etc. (right figure)
  - Enormous light absorption by some of these: huge potential for photochemistry
  - FF ~ brine > Nilas ~ sea water >> sea ice ~ terrestrial surface snow
 - CDOM likely dominant chromophore; links microbes with photochemistry

One typical terrestrial snow

Marine samples
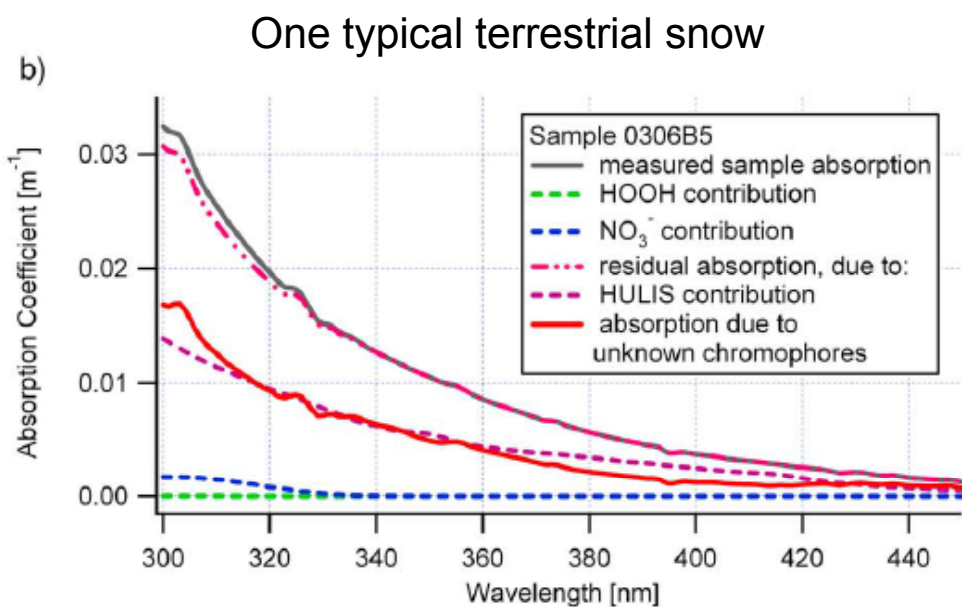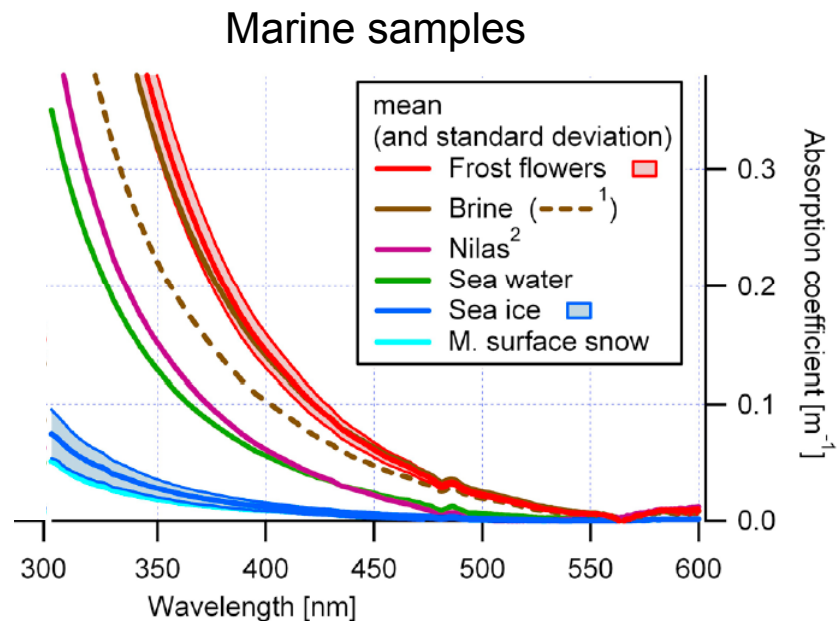
Beine et al., JGR, 2011

Beine et al., JGR, 2012

Singlet Molecular Oxygen ($^1O_2$*)

- What are likely products from CDOM/HULIS/humics photochemistry?
  - ^3C* (excited triplet states)
  - $^1O_2$* (singlet molecular oxygen), an excited (more reactive) form of O_2
  - Other: OH, VOCs, other…

- $^1O_2$* formation steps
  - Sensitizer such as CDOM absorbs light to become triplet state (^3C*)
    - We are using Rose Bengal (RB) as a model sensitizer
  - ^3C* transfers energy to O_2 to make $^1O_2$*
  - $^1O_2$* can oxidize electron-rich organics (PAHs, furans, phenols, sulfides…)
  - ^3C* might also oxidize organics
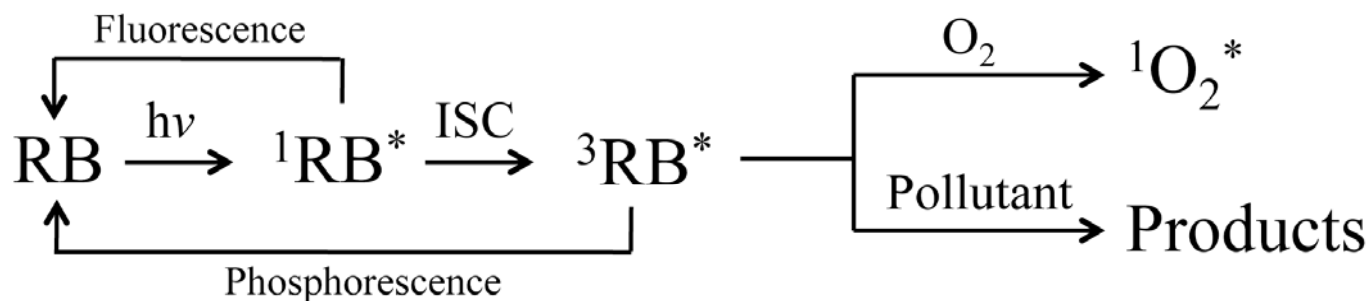
$^1O_2$* Enhanced on Ice Compared to Liquid

- Method

  - Make solutions with sensitizer (RB), $^1O_2$* probe (furfuryl alcohol, FFA), and salt to adjust total solute (TS) conc

  - Illuminate (549 nm); monitor FFA loss

  - Study as solution and ice pellets

  - Normalize results to photon fluxes

- Example of results

  - Conditions here:

    250 µM Na_2SO_4, 10 nM RB, –10°C ice

  - Kinetic plots for loss (top)

  - Photon-normalized rate constants (bot)

  - *Freeze-concentration factor,*

    F ≈ k(ice) / k(solution)

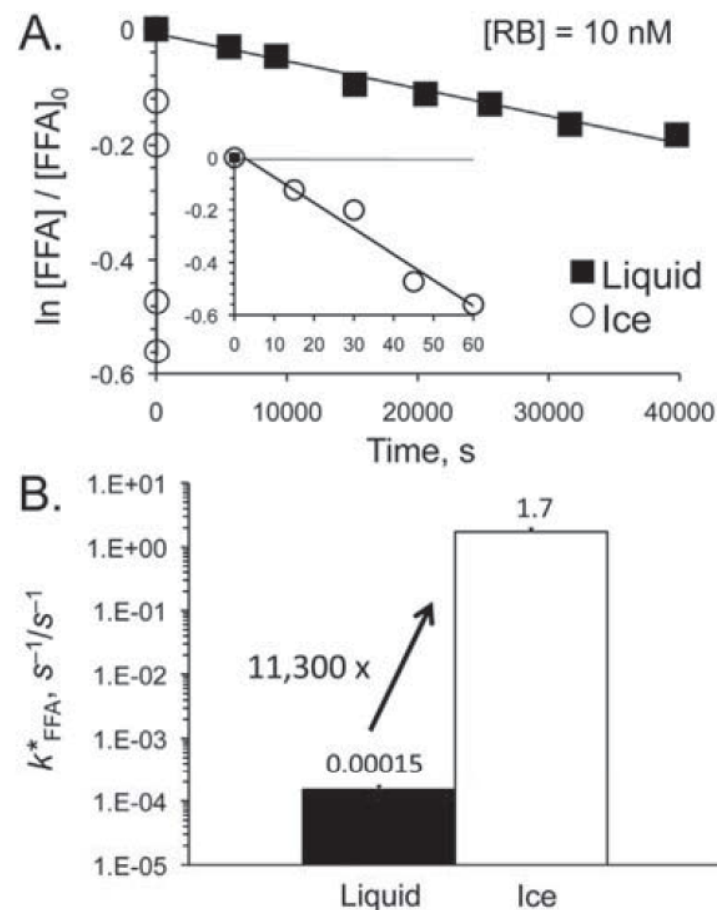 - *F ≈ 11,300 in this case*

Bower and Anastasio, Atm Env, 2013

Fig. 1. (A) First-order plots for loss of furfuryl alcohol in a liquid sample (1.0 µM FFA, 5 °C) and ice sample (0.10 µM FFA, −10 °C). The inset shows details of FFA decay in the ice sample. Both samples contained 250 µM total solutes (TS) as Na_2SO_4 and 10 nM Rose Bengal (RB) and were illuminated with 549 nm light. (B) Calculated first-order rate constants for loss of FFA (normalized to photon flux, which results in units of s^{-1}/s^{-1} (Equation (1a))) calculated from the data in panel (A). The rate constant for FFA loss on ice is 11,300 (±2200) times higher than the value in the liquid sample.

Using $^1O_2^*$ to Measure Freeze-Concentration Factors

- NaCl above T_{eu}
  - Good agreement between expt and FPD
  - Strong dependence on [TS]: implications

- NaCl below T_{eu}
  - All salt should be precipitated
  - But still evidence for LLR chemistry and dependence on [TS]
  - Cho et al. and Grannas et al. also saw evidence for LLRs below T_{eu}

- $[^1O_2^*]$ can be greatly elevated on ice
  - Significant oxidant for organics on snow/ice?

- We also find $[^3C^*]$ elevated on ice
  - Data not shown
  - Is it a significant oxidant on snow/ice?
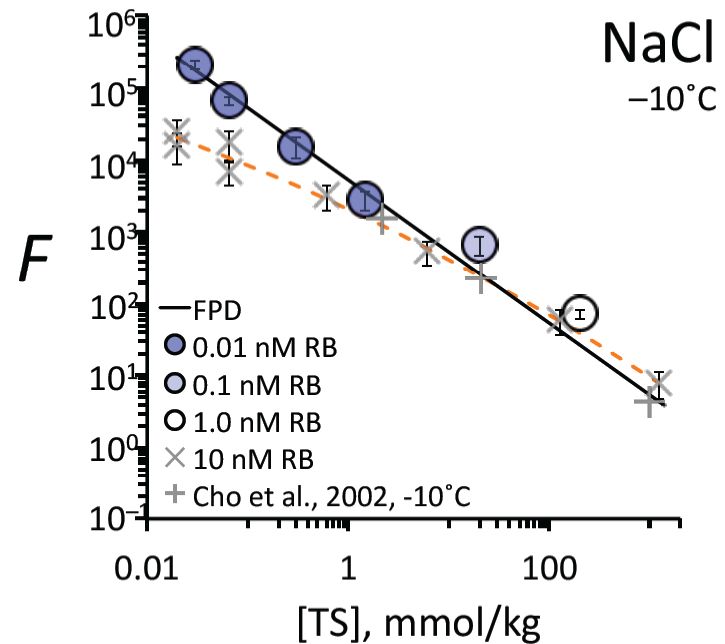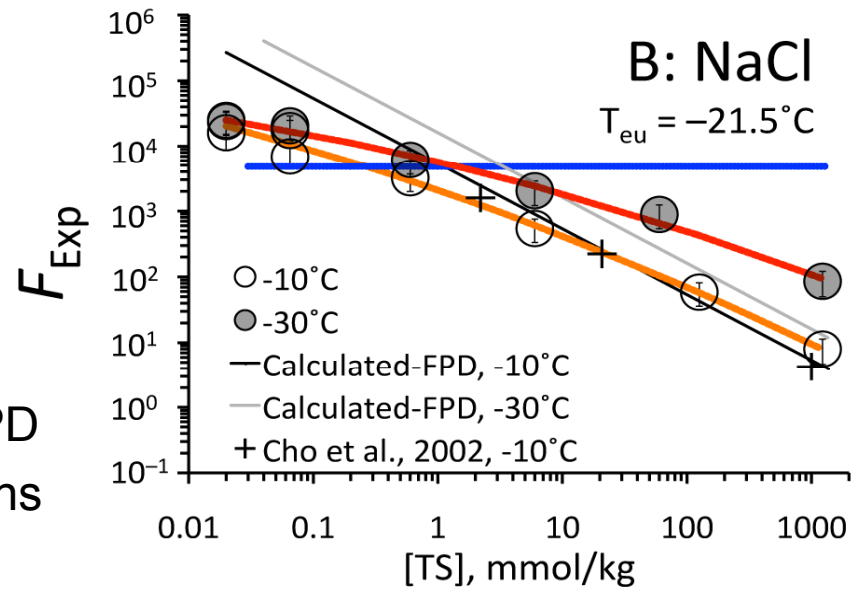
How to Model Pollutant Oxidation in LLRs?

- Oxidation rate for pollutant P equals sum of its individual pathway rates:

  Rate of Loss of P = Rate from OH + Rate from $^1O_2^*$ + Rate from $h\nu$ + ...

  $L_P = k_{OH+P}[OH][P] + k_{1O2^*+P}[^1O_2^*][P] + j_P[P] + ...$

- Some complications
  - Relative to melted sample, some oxidants are enhanced in LLRs (e.g., $^1O_2^*$) while others are not (e.g., OH)
  - Need to consider air-ice partitioning and precipitation for *P*
  - Direct photodegradation (j_P) might be different in LLRs compared to solution based on Tara and Jamie's QLL work

- A framework for snow/ice photochemistry
  - If chemistry in other reservoirs (QLL, bulk ice, PM...) is important for a given compound or process...
  - ...and if chemistry in that reservoir is different from in the LLR...
  - ...then add rate of loss in each reservoir...

    $L_{P,ICE} = L_{P,LLR} + L_{P,QLL} + L_{P,BULK} + ...$
  - LLR chemistry seems similar to super-cooled liquid; QLL not; bulk ice?
  - For simplicity, let's hope not all reservoirs are significant for chemistry

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Thoughts on a Future Field Campaign

- Paul says "go up". I say "*Get Down*" (cue disco music)

- What is occurring in the snowpack? We need…
  - Firn air measurements (HO_x, HCHO, HOOH, O_3, NO_x, light, met.…)
  - Snow grain measurements (pH, Org C, Br-, HOOH, NO_2^-, NO_3^-…)
  - Rates of oxidant formation on snow grains
  - Modeling

- A science question that interests me: What are the possible impacts of decreased snow/ice extent on oxidation chemistry?
  - Less OH formation: $\downarrow Br^-$ oxidation $\rightarrow$ $\downarrow O_3$ depletion and $\downarrow$Hg oxidation
    $\downarrow$ oxidation of deposited Org C (POPs, Org PM…)
  - Less $^1O_2^*$ and $^3C^*$: $\downarrow\downarrow$ Org C processing?
  - Are there feedbacks between oxidants and microbes?
    - CDOM is probably major source of $^3C^*$ and $^1O_2^*$
    - Do oxidants ($^3C^*$, $^1O_2^*$, OH, HOOH…) alter microbe output?