# Exploring new pathways on ice

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**Department of Chemistry**
**University College Cork**

3rd workshop on Air-Ice Chemical Interactions (AICI):
New York, USA. June 2011

# With thanks to………..

- Daniel O’Sullivan*
- Ruairi O’Concubhair*
- Ryan McLaughlin, Kevin Clemitshaw
- Paul O’Driscoll
- David O’Connor
- Tom Koch
- Nick Holmes
- Tristan Roddis
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- Science Foundation Ireland, EU Marie Curie
- Faye and Thorsten!

# Understanding the Atmosphere….

**Phase 1**

FIELD

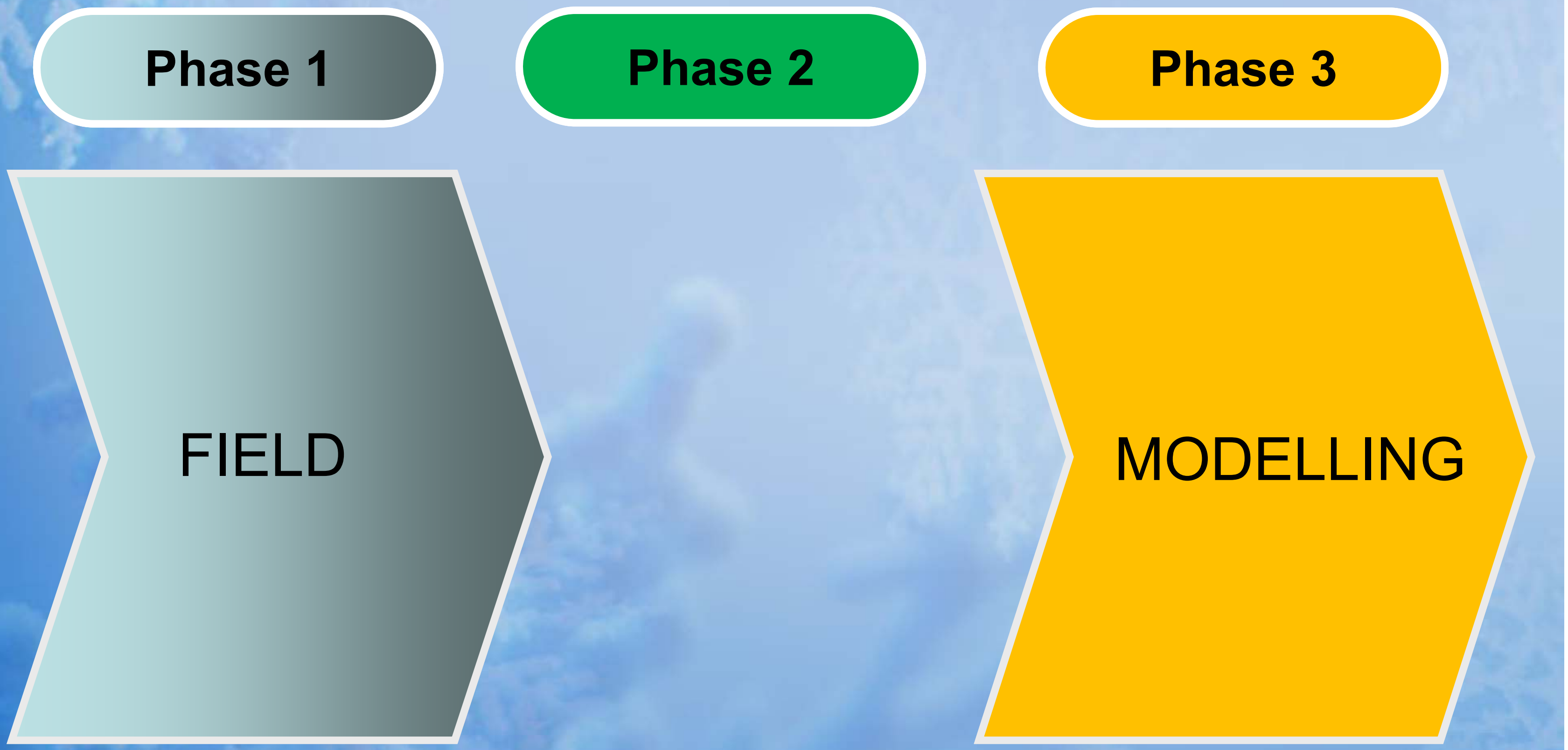
**Phase 2**

LABORATORY

**Phase 3**

MODELLING

# ….needs a Laboratory Bridge



**Phase 1**

**Phase 2**

**Phase 3**

FIELD

MODELLING

**Recognising possibilities in order to help predict behaviours**

# What drives the laboratory studies?

Field observations

Measurement of ice physico-chemical properties

The search for “missing” chemistry in the models

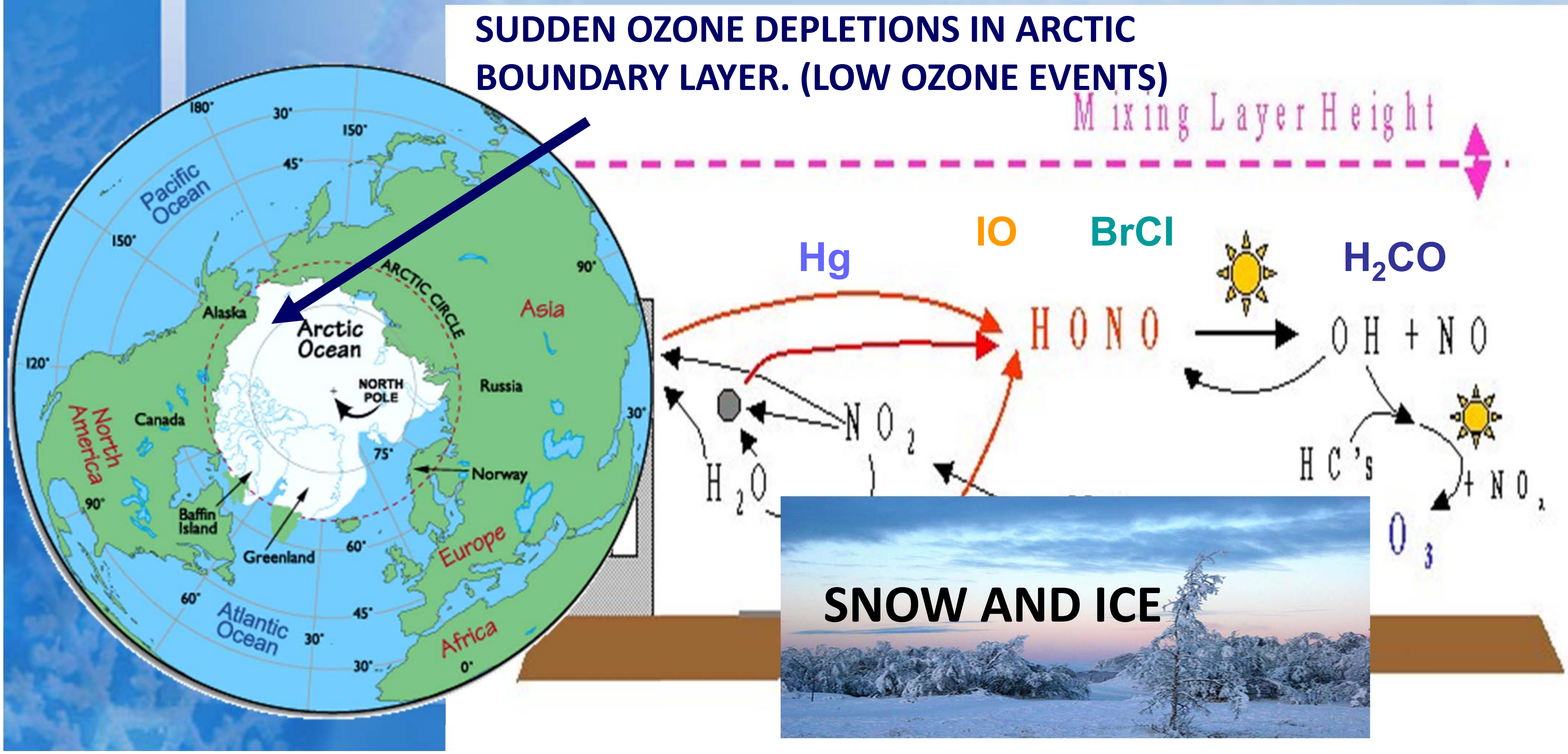
The discovery of unexpected pathways on ice

# What drives the laboratory studies? What's occurring?

**Field observations**

# Atmospheric Cryochemistry: Surface Emissions at the Poles

- The Arctic atmosphere suffers from air pollution episodes that are more commonly experienced in urban environments!



**SUDDEN OZONE DEPLETIONS IN ARCTIC BOUNDARY LAYER. (LOW OZONE EVENTS)**

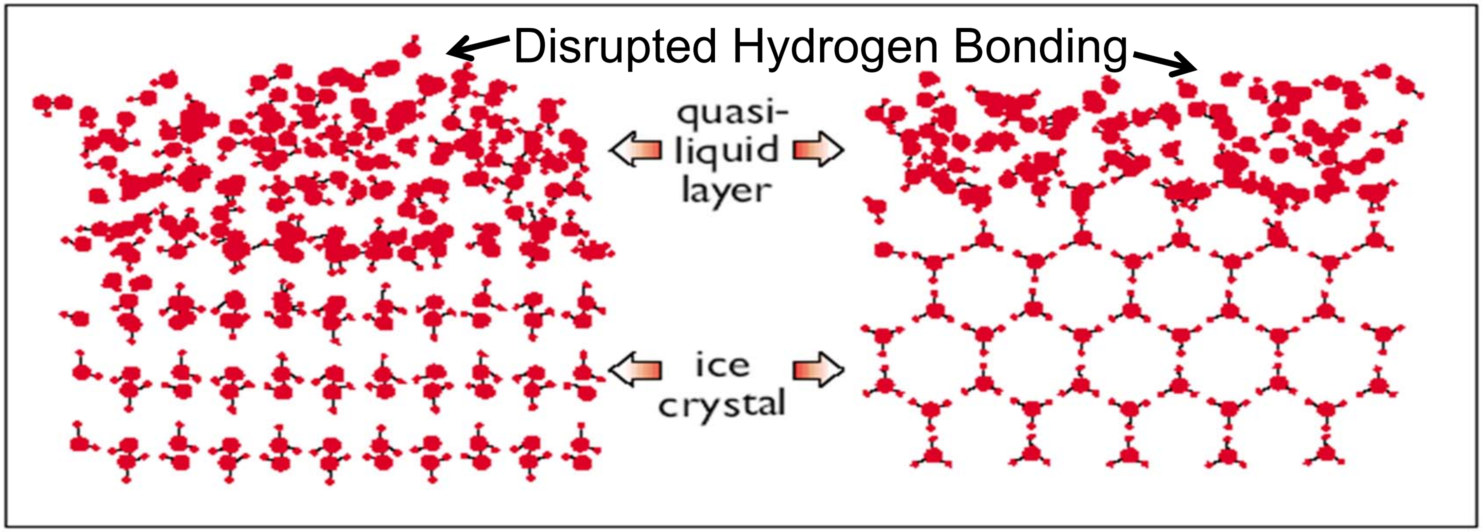
**SNOW AND ICE**

# What drives the laboratory studies?
# Where's it occurring?

**Measurement of ice physico-chemical properties**

# The Quasi Liquid Layer (QLL)

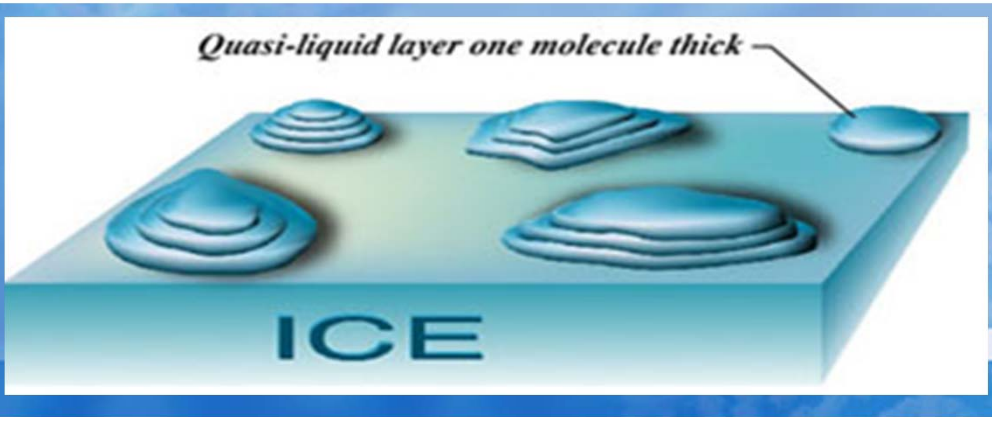
## (Originally predicted by Michael Faraday in 1859)



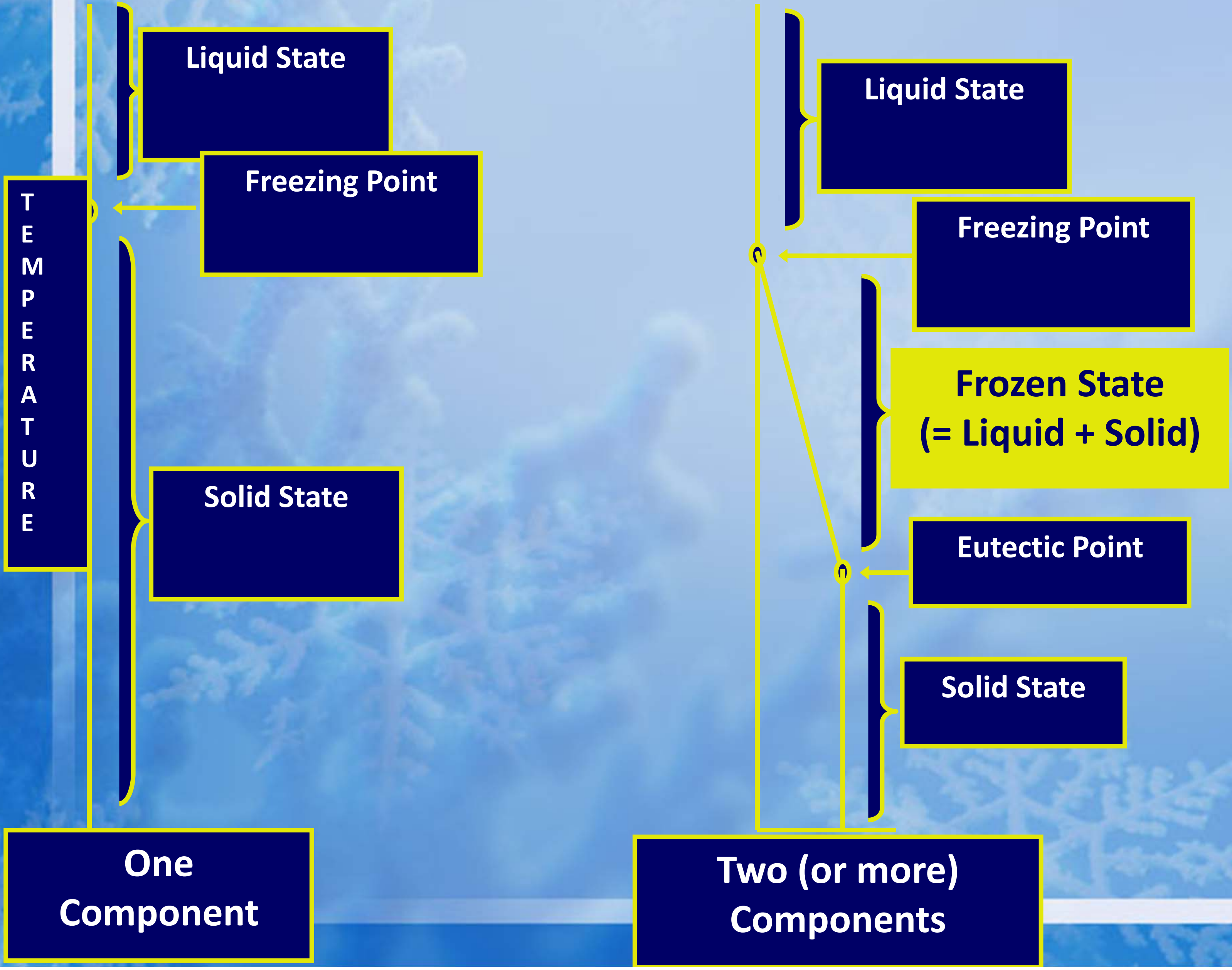
A quasiliquid layer forms on the surface of ice when water molecules at the edges of the crystal jostle loose from the tightly bound inner lattice. The thickness of this layer depends on temperature and is generally different for the basal (left) and prism (right) crystal faces.

**QLL**

**ISLANDS**



# Water-ice Matrix “Micropockets”



TEMPERATURE

Liquid State

Freezing Point

Solid State

One Component

Liquid State

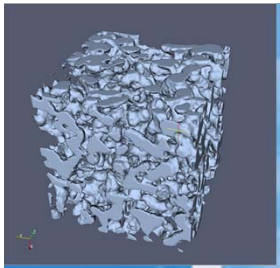
Freezing Point

Frozen State (= Liquid + Solid)

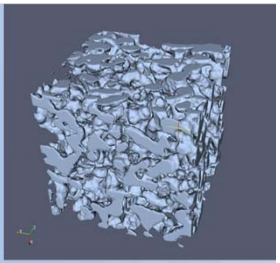
Eutectic Point

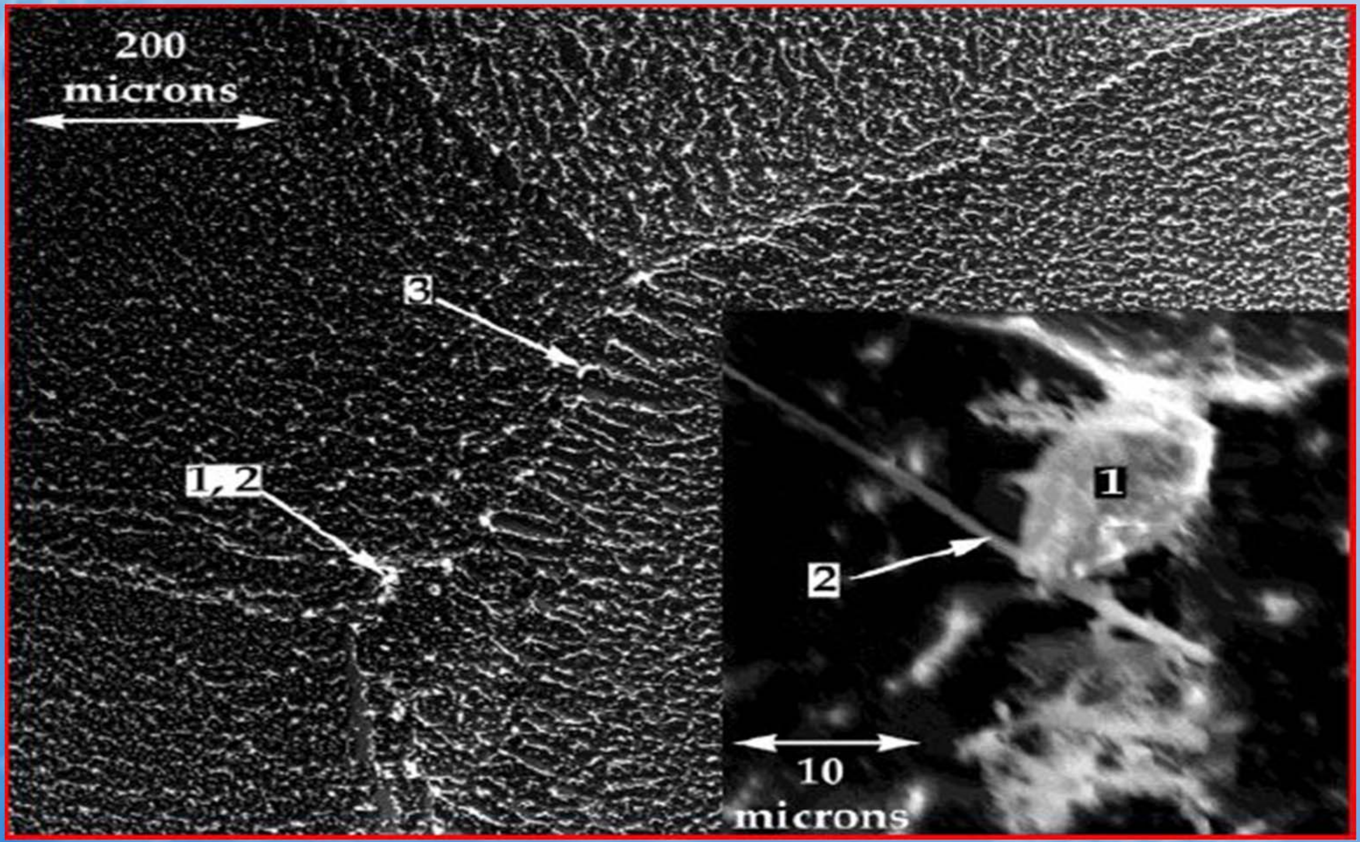
Solid State

Two (or more) Components



# Micropockets or Microveins: Triple Junctions to Ice Physicists





Liquid regions with areas <10 $\mu m^2$ have been measured by microscopy in ice crystals at 253K (Matsuoka et al *Journal of Physical Chemistry B* 1997, *101*, 6219-6222).

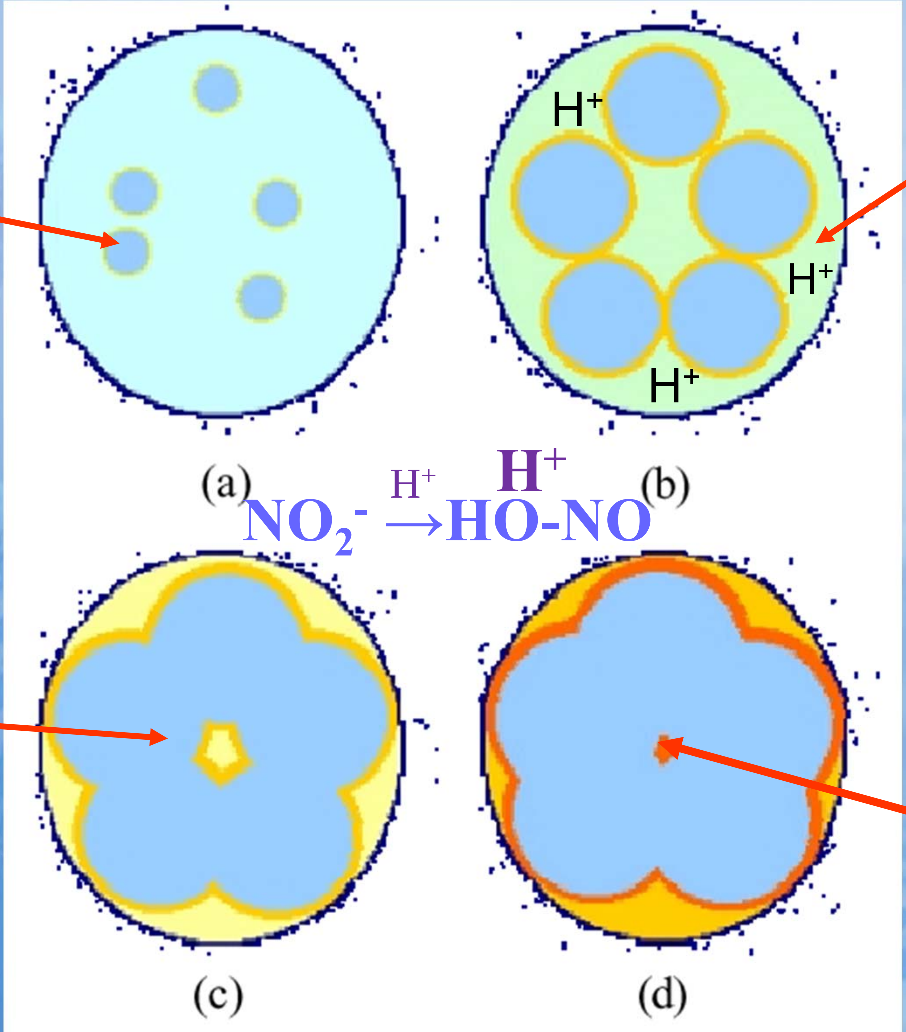
# What drives the laboratory studies?
# Why's it occurring?

**The search for "missing" chemistry in the models**

# Freeze-concentration and freezing potentials increasing acidity in water-ice micropockets

Single ice crystals begin to grow

Protons rejected into liquid phase as crystals grow



Further ice growth confining solute and concentrating it

High concentrations lead to accelerated reaction in "micropockets" and QLL

N. Takenaka, T. Daimon, A. Ueda, K. Sato, M. Kitano, H. Bandow and Y. Maeda, *J. Atmos. Chem.* , 1998, **29**, 135-150.

# What drives the laboratory studies? How's it occurring?

**The discovery of unexpected pathways on ice**

The influence of freezing on dilute aqueous solutions containing halide ions

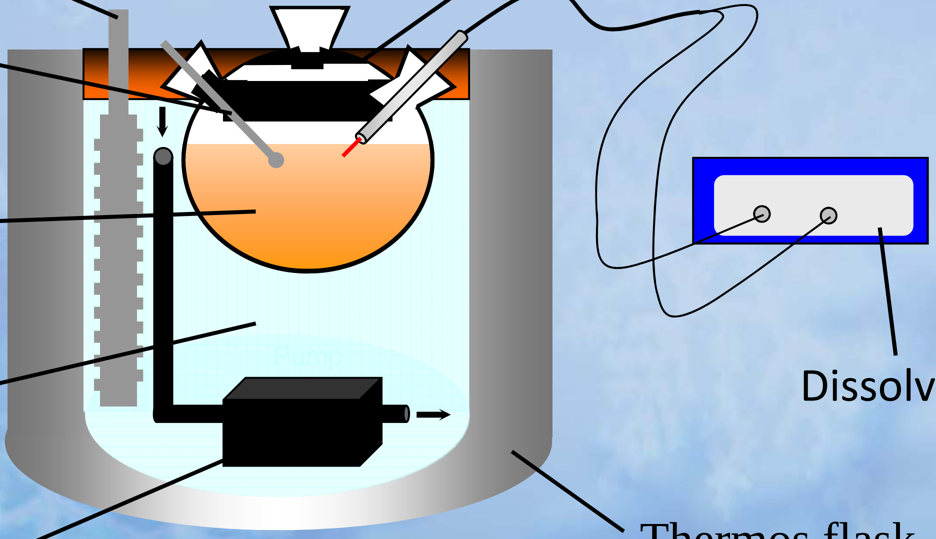
The low-temperature photochemical reactivity of nitrates on/in thin water-ice films

The low-temperature chemical reactivity of sulfur dioxide on/in thin water ice films

Dark oxidation of dissolved gaseous mercury (DGM) in ice

**Recognising possibilities in order to help predict behaviours**

# The influence of freezing on dilute aqueous solutions containing halide ions



**Cryocool to -30°C**

Round-bottomed flask

Thermocouple

**Acidified aqueous $I^- / NO_2^- / Br^-/Cl^-$ solution**

Dissolved $O_2$ Sensor

Ethanol Bath

Thermos flask

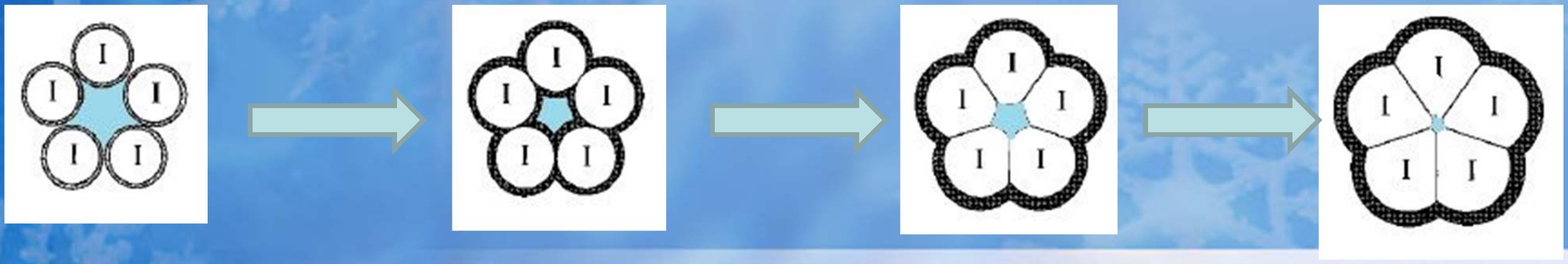
Pump

**HP8453 UV/Vis Diode Array Spectrometer**

# Freeze-induced Chemistry

$$2I^- + 2HONO + 2H^+ \longrightarrow 2NO + I_2 + 2H_2O$$

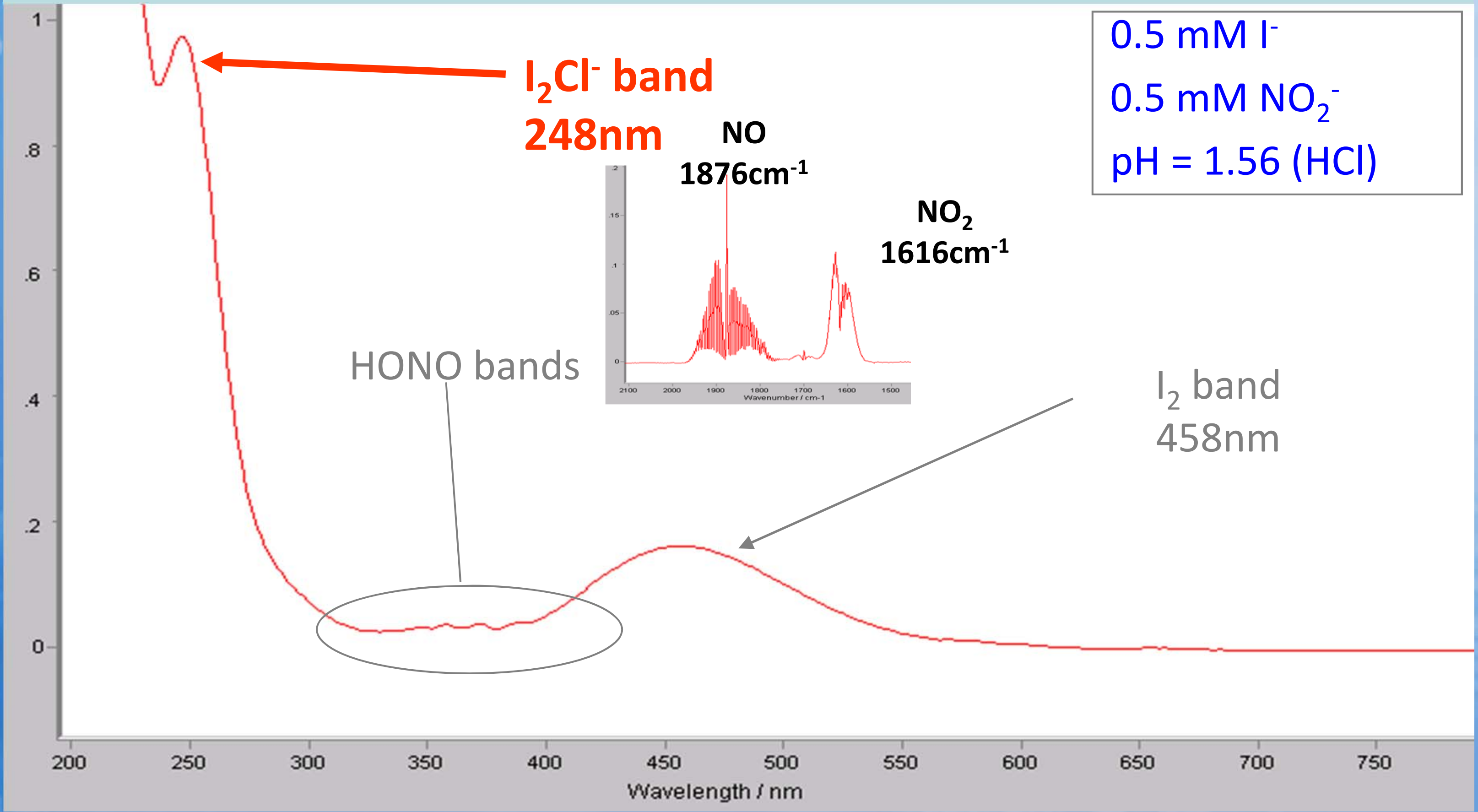
- At pH>5.5, reaction is negligible in room temperature solution
- Dissolved oxygen likely plays a “catalytic” role
- Complex reaction mechanism
- Reaction orders are high: 4-6
- **Accelerated > 400x upon freezing**



# $I^-$ / $NO_2^-$ / HCl at Room Temperature

## $I_2$ , HONO and $I_2Cl^-$ are generated before freezing

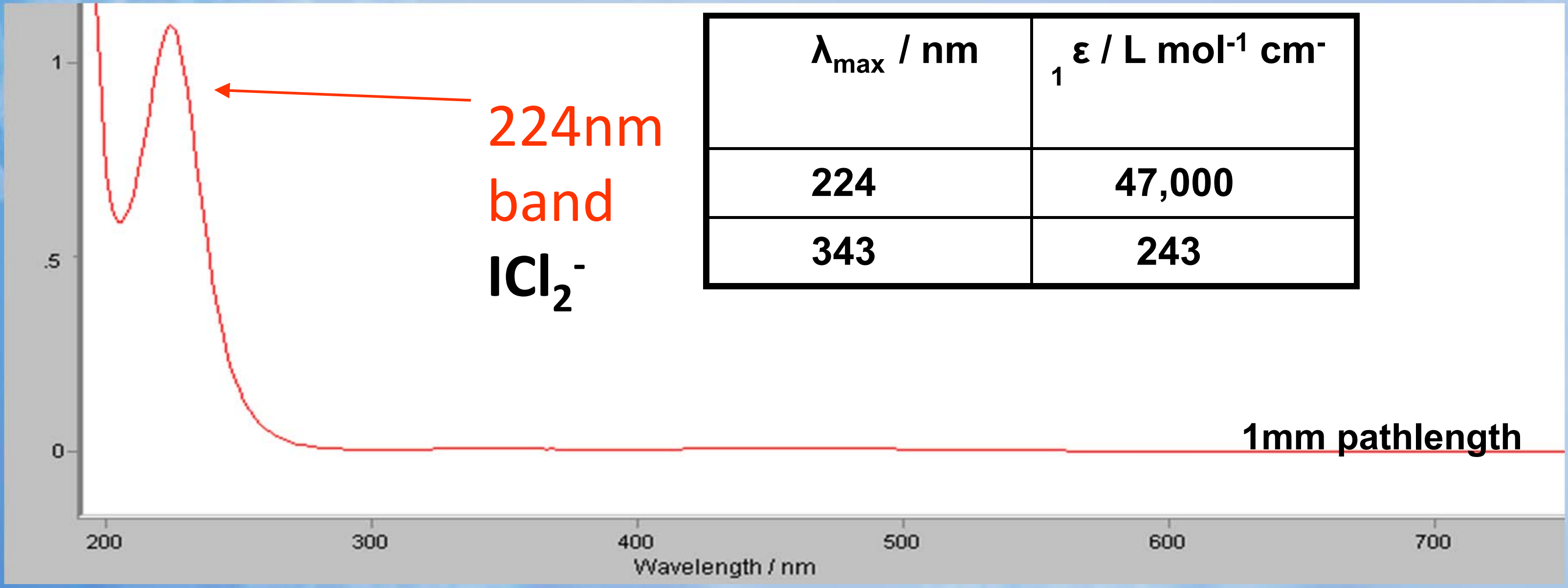
P. O'Driscoll, N. Minogue, N. Takenaka and J. Sodeau,
*J. Phys. Chem. A*, 2008, **112**, 1677-1682.



0.5 mM $I^-$
0.5 mM $NO_2^-$
pH = 1.56 (HCl)

## Unusual transformation after freeze-thaw

# After Freezing: $ICl_2^-$ appears

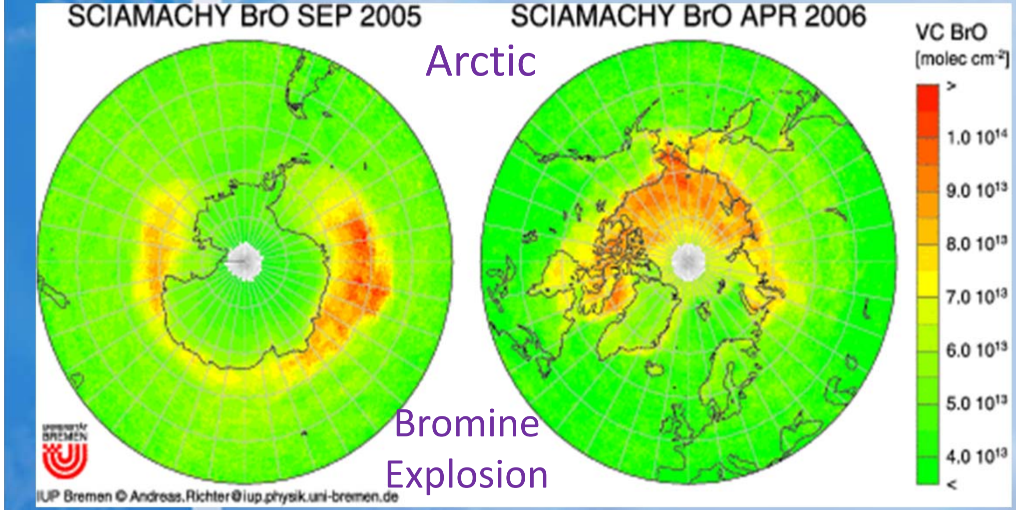


| $\lambda_{max}$ / nm | $\varepsilon$ / L mol$^{-1}$ cm$^{-1}$ |
|---|---|
| 224 | 47,000 |
| 343 | 243 |

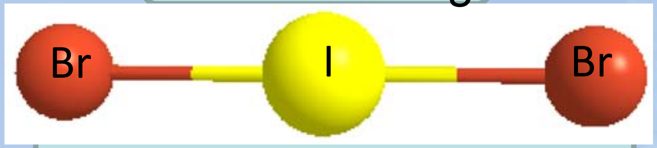
- Reaction also works if $Cl^-$ replaced with $Br^-$
- For $[X^-]: [I^-] = 10:1$
- Relatively low pH chemistry *i.e.* pH < 2.8

P. O'Driscoll, K. Lang, N. Minogue and J. Sodeau,
*J. Phys. Chem. A*, 2006, **110**, 4615-4618.

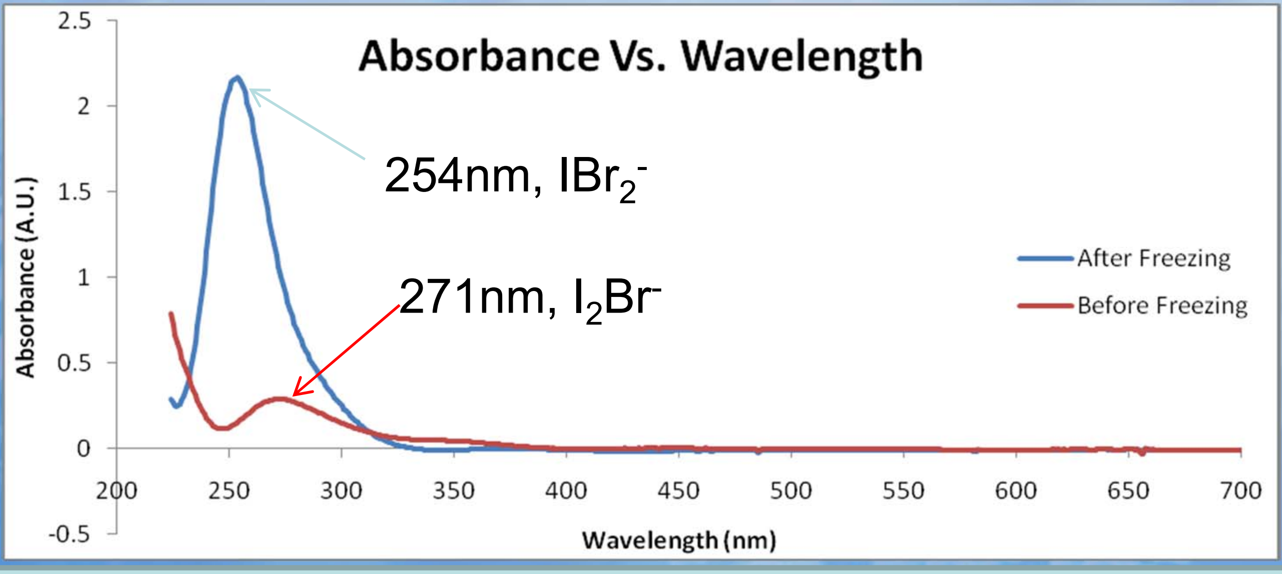
# The atmospheric importance of $IBr_2^-$



Weak Bonding



$$IBr_2^- \rightleftharpoons IBr_{(aq)} + Br^-$$



254nm, $IBr_2^-$

271nm, $I_2Br^-$

$IBr_{(aq)} \leftrightarrow IBr_{(g)}$

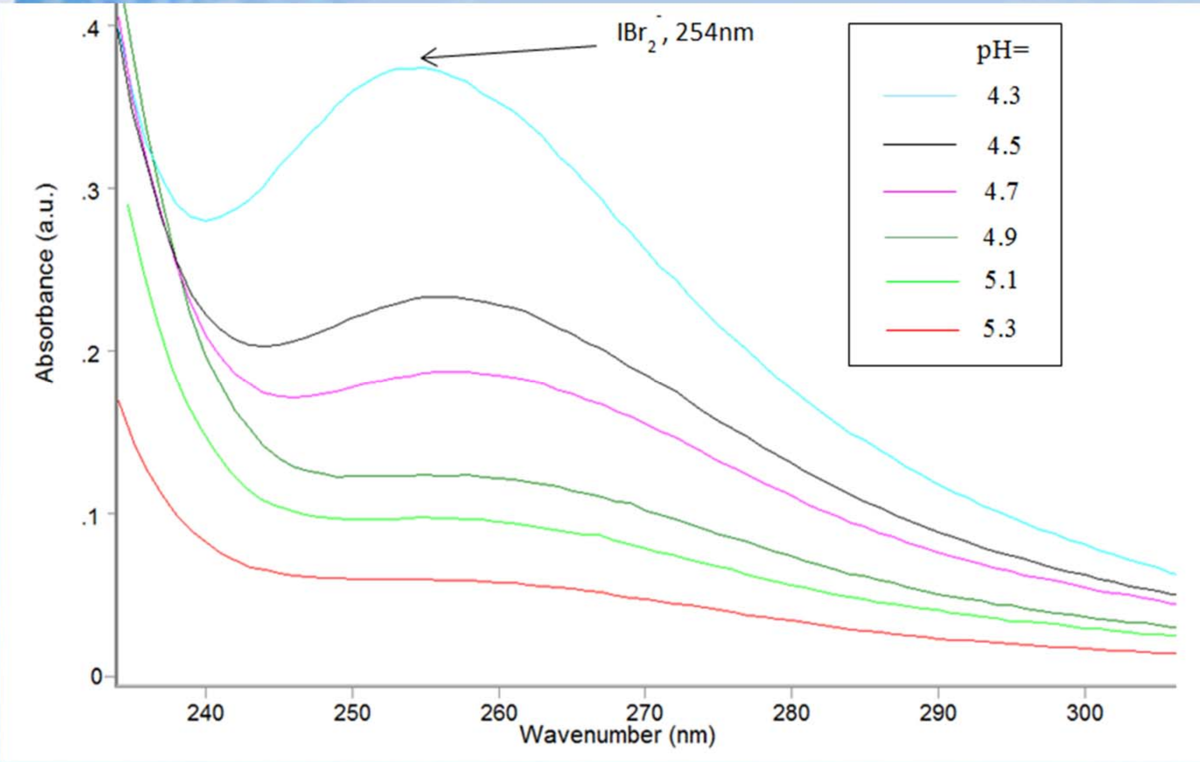
$IBr + h\nu \rightarrow I + Br$

$Br + O_3 \rightarrow BrO + O_2$

Can reaction be manipulated to work at environmentally relevant pH and concentrations?

# Is feidir linn!

For $[Br^-]:[I^-]$ = 6160:1 (i.e. as in seawater) the reaction proceeds up to pH 5.3

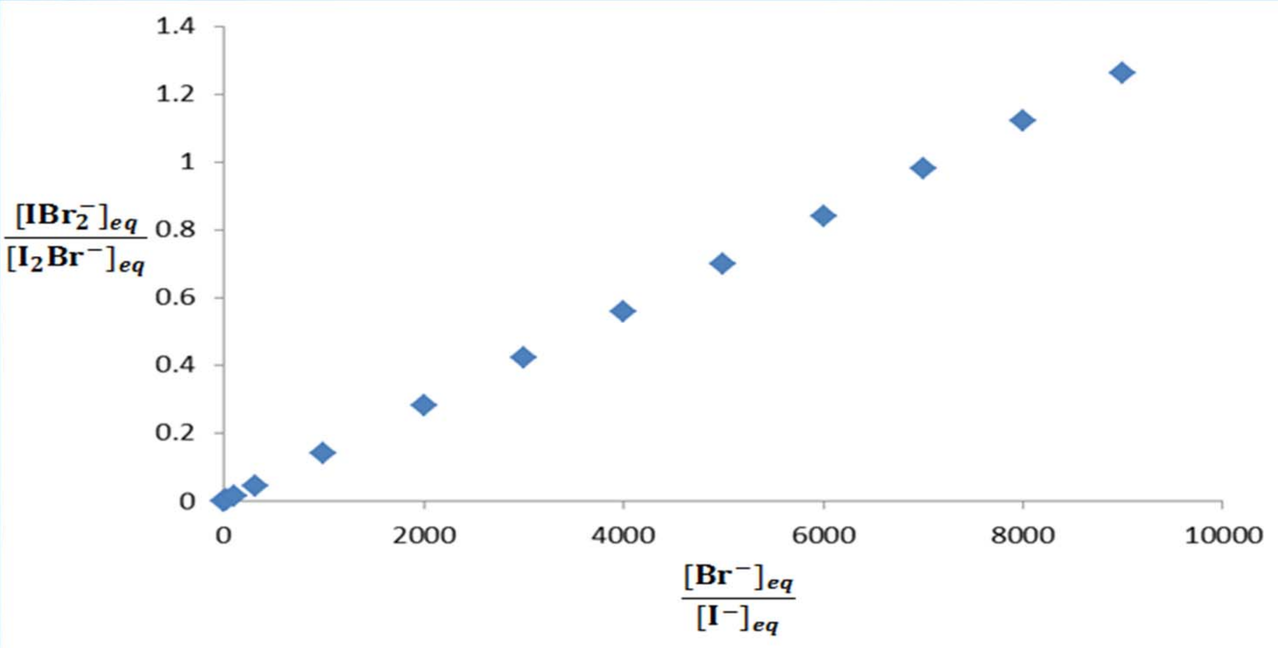


HONO ($H_2ONO^+$) are not the only oxidants capable of driving these types of reaction: $H_2O_2$ also works

Freeze-Induced Reactions: Formation of Iodine-Bromine Interhalogen Species from Aqueous Halide Ion Solutions.
D O'Sullivan and J Sodeau. J Phys Chem A 114 12208-12215 2010

# Mechanism

$I_2Br^- + Br^- \rightleftharpoons IBr_2^- + I^-$ $K_{eq} = 1.4 \times 10^{-4}$



- Higher pH condition possible when $[Br^-] : [I^-]$ ratio increased
- $I^-$ is a strong antagonist towards $IBr_2^-$ formation
- The oxidation agent (HONO, $H_2ONO^+$, $H_2O_2$) heavily depletes the amount of free $I^-$ during the freezing process

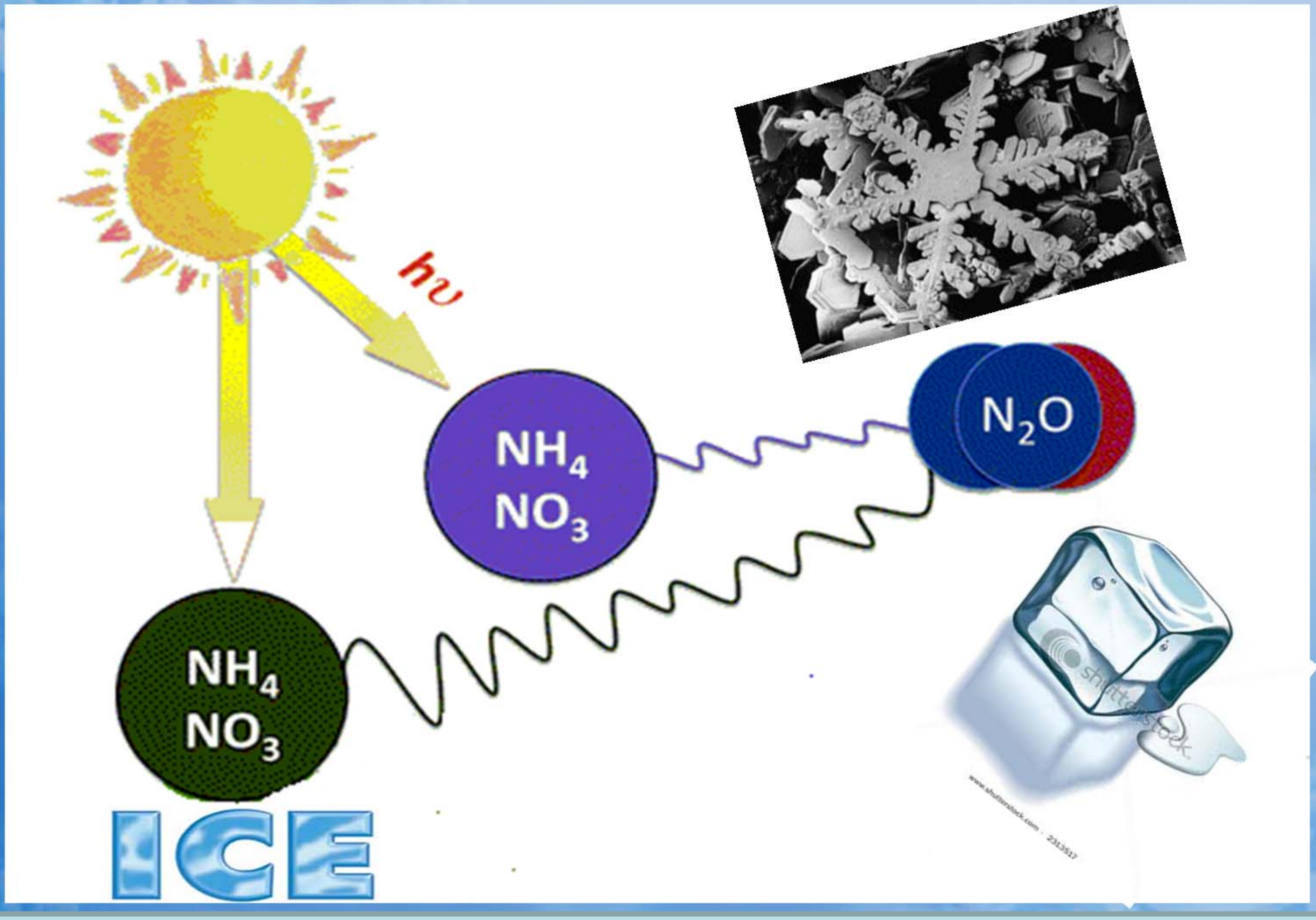
# The low-temperature photochemical reactivity of nitrates on/in thin water-ice films

Environ. Sci. Technol. 2011, 45, 2691–2697

Abiotic Mechanism for the Formation of Atmospheric Nitrous Oxide from Ammonium Nitrate. Gayan Rubasinghege, Scott N. Spak, Charles O. Stanier, Gregory R. Carmichael, and Vicki H. Grassian

# The low-temperature photochemical reactivity of organo-nitrates on/in thin water-ice films

J.Phys Chem A. **1996**, 100, 11402–11407

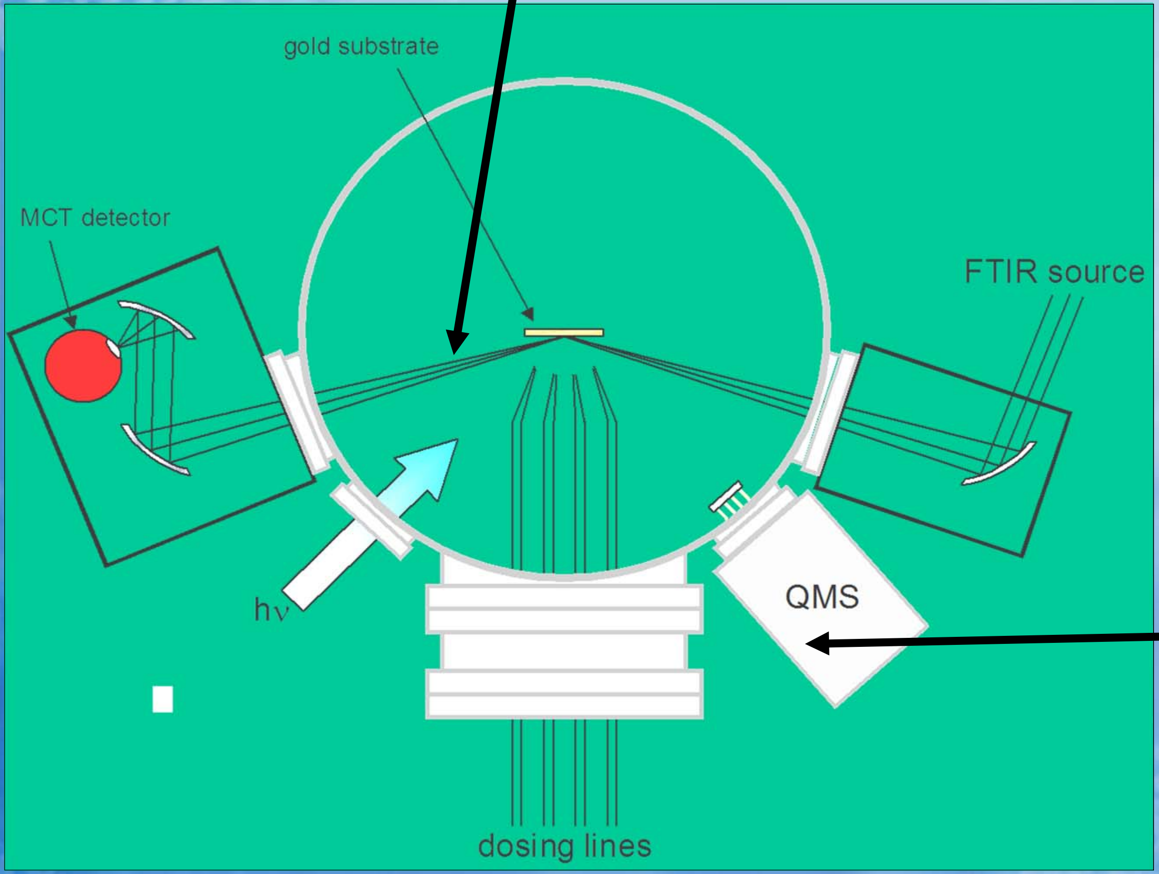


$N_2O$ is not controlled by Montreal Protocol as an ozone destroyer

**Low-temperature photochemistry of submicrometer nitric acid and ammonium nitrate layers. Tom Koch, Nick Holmes, Tristan Roddis and John Sodeau**

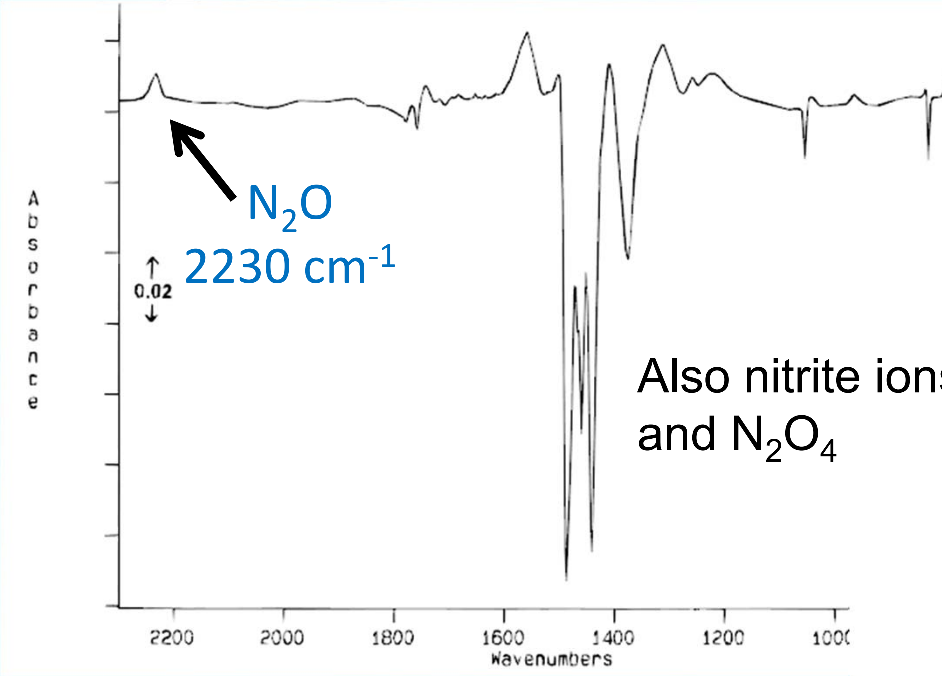
# FT-RAIRS/TPD investigations of nitrates on water-ice films

**FTIR ANALYSIS OF SURFACE SPECIES ON WATER-ICE**



**MASS SPECTROMETRY (THERMAL PROGRAMMED DESORPTION) FOR ANALYSIS OF GAS-PHASE RELEASED PRODUCTS**

# Photolysis of ammonium nitrate on water-ice to produce $N_2O$



$N_2O$
2230 $cm^{-1}$

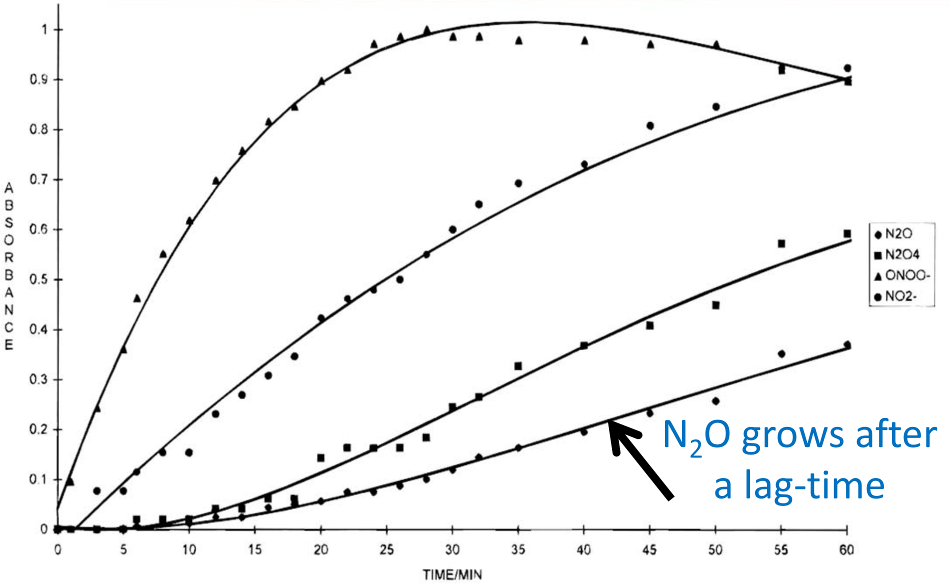
Also nitrite ions and $N_2O_4$

$$NO_3^- + h\nu \rightarrow NO_2 + O^-$$
$$NO_3^- + h\nu \rightarrow NO_2^- + O$$

STEP 1

$$NH_4^+ + O^- \rightarrow NH_2 + H_2O$$
$$NH_2 + NO_2 \rightarrow N_2O + H_2O$$

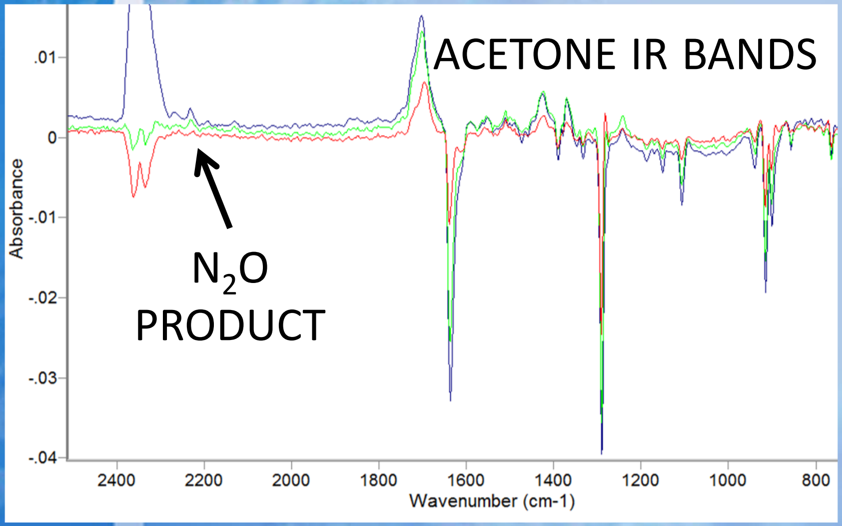
STEP 2



Normalized kinetic profiles of $ONOO^-$, $NO_2^-$, $N_2O$, and $N_2O_4$ produced upon ammonium nitrate photolysis.

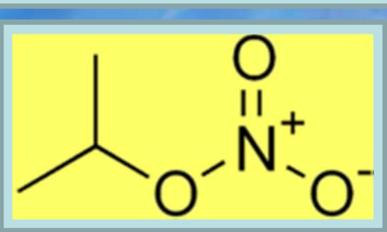
$N_2O$ grows after a lag-time

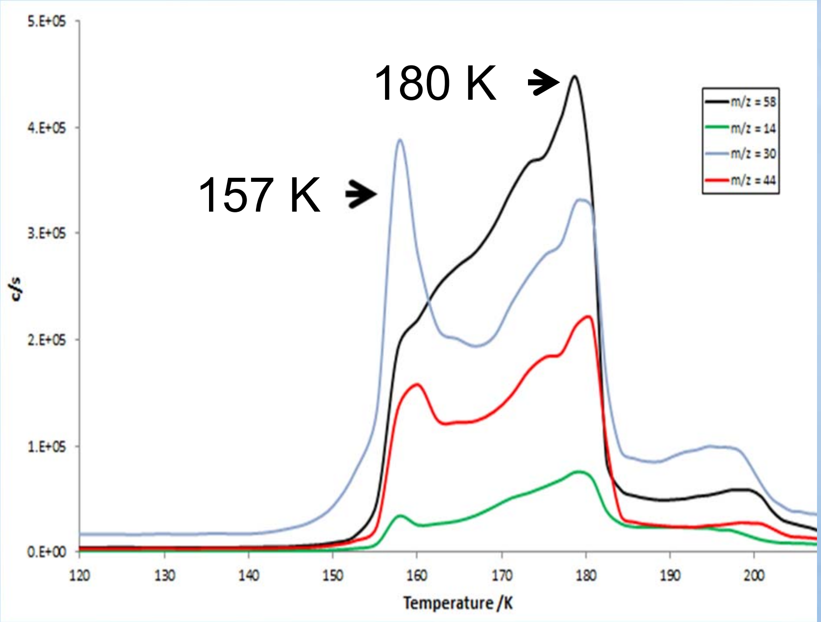
# Photolysis of alkyl nitrates on ice to produce $N_2O$



ISOPROPYL NITRATE PHOTOLYSIS

$\lambda > 300$ nm for 1, 2 and 3 h



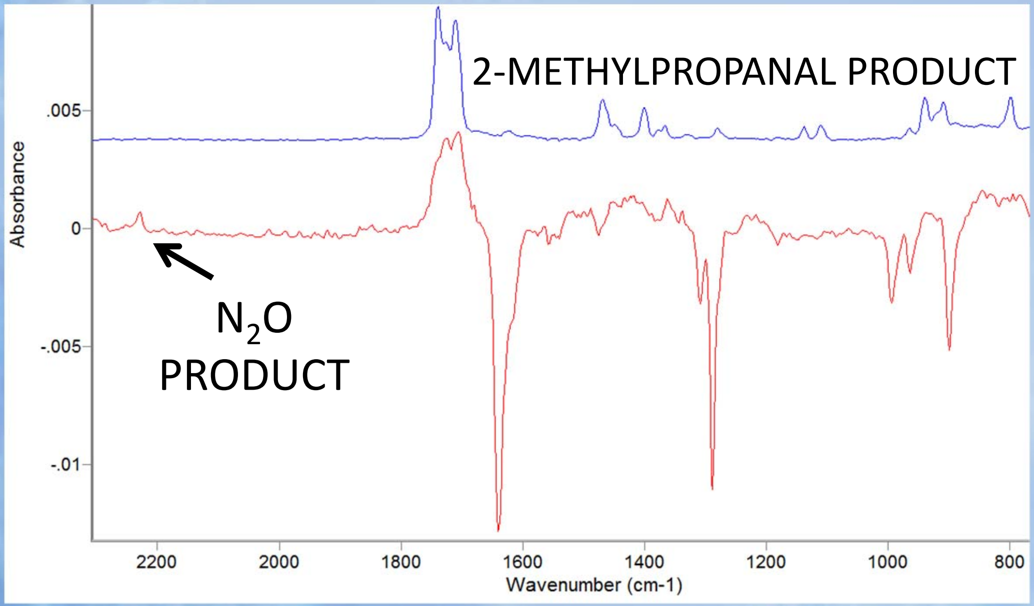


TPD showing:

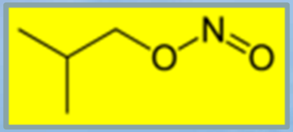
m/z = 44, 30 and 14 ($N_2O$)

m/z = 58 (ACETONE)

# Photolysis of alkyl nitrates on ice



ISOBUTYL NITRATE
PHOTOLYSIS $\lambda$>300 nm



- The relative photolysis rates of the three alkyl nitrates investigated were found to mimic those in the gas-phase.
- They increase in the order (R= Me < *i*-Pr < *i*-But).
- PAN did not appear to photolyse at all on ice with $\lambda$>300 nm!

# What is the generalised mechanism to explain this?

$$RONO_2 + h\nu \longrightarrow R'CH_2O^{\bullet} + NO_2$$

$$NO_2 + h\nu\ (\lambda < 420\ \text{nm}) \longrightarrow NO + O(^3P)$$

$$R'CH_2O^{\bullet} + NO \longrightarrow R'CH_2ONO$$

**Promoted in a frozen matrix**

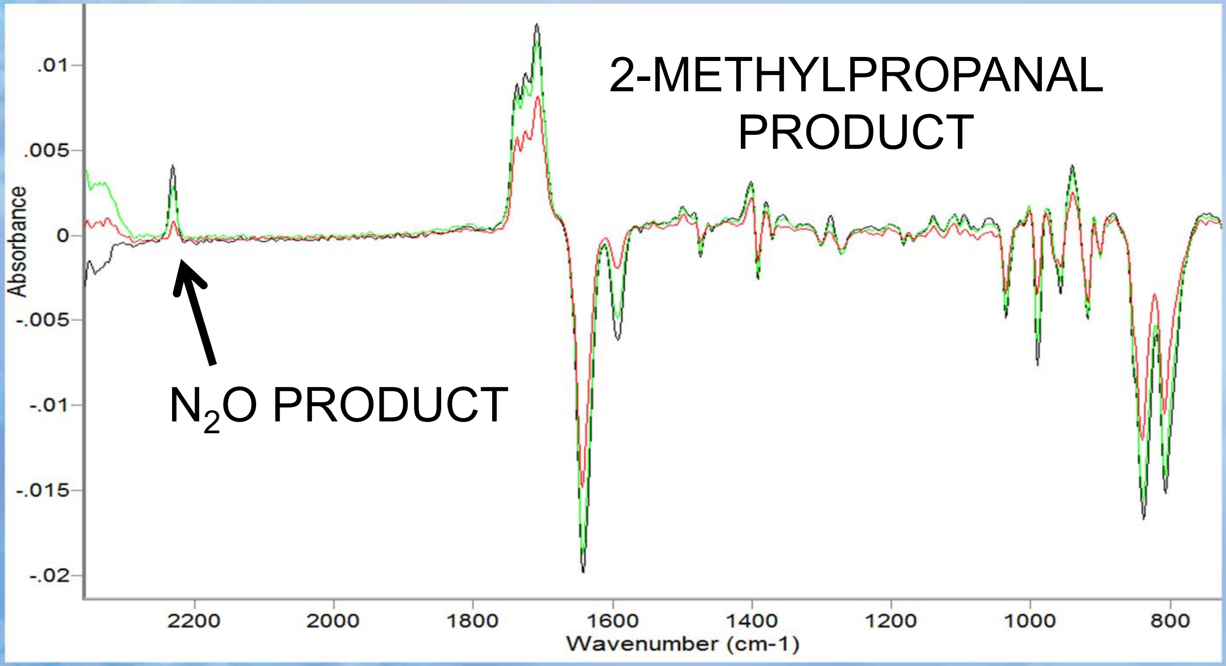
$$RCH_2ONO + h\nu \longrightarrow RCH_2O + NO$$

ALKYL NITRITE INTERMEDIACY!

$$RCH_2O + NO \longrightarrow RCHO + HNO$$

$$2HNO \longrightarrow N_2O + H_2O$$

# Photolysis of alkyl nitrites on ice

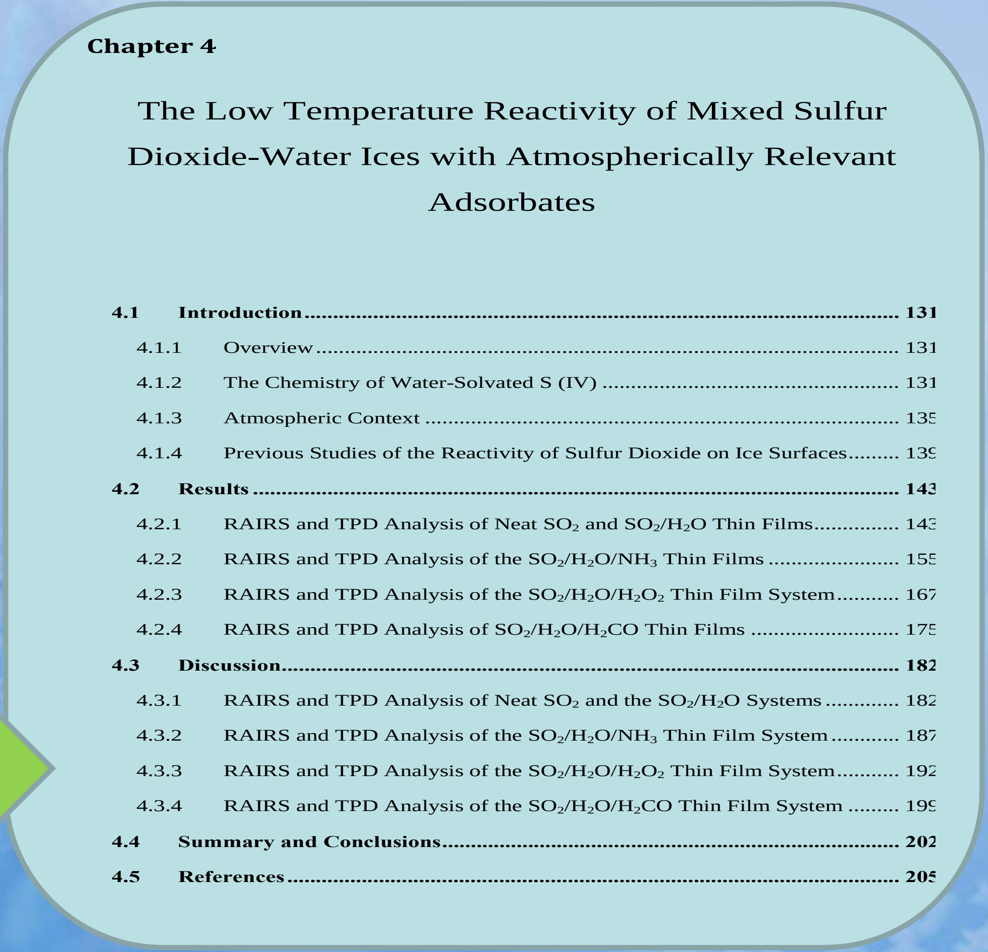

2-METHYLPROPANAL PRODUCT

$N_2O$ PRODUCT

ISOBUTYL NITRITE

PHOTOLYSIS $\lambda$>300 nm

# The low-temperature chemical reactivity of sulfur dioxide on/in thin water-ice films



**Chapter 4**

## The Low Temperature Reactivity of Mixed Sulfur Dioxide-Water Ices with Atmospherically Relevant Adsorbates

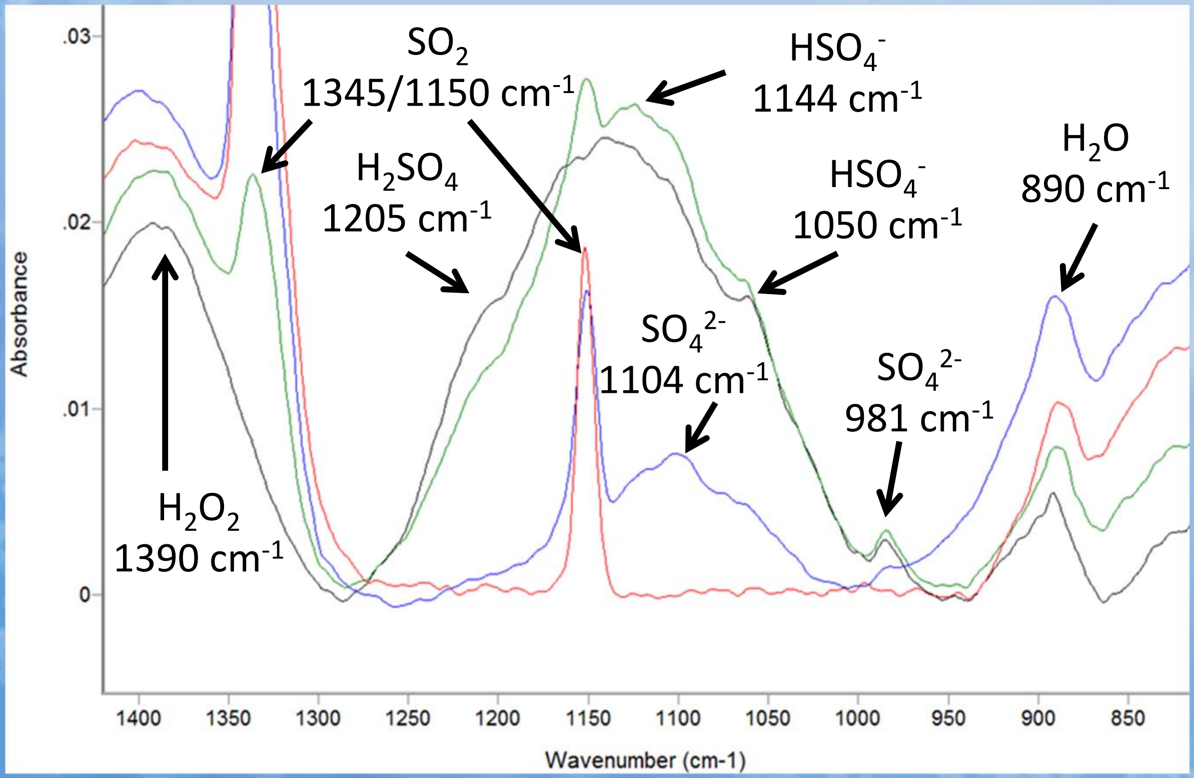
+$H_2O_2$

Daniel O'Sullivan. PhD Thesis. UCC. (2011)
A study of water-ice mediated Chemical Processes Relevant to the Troposphere

# S(IV) to S(VI) oxidation in water-ices

$SO_2/H_2O_2/H_2O$ co-deposition at 120 K and then annealed to 170 K, 180 K and 190 K

**RAIR Spectra**



170 K

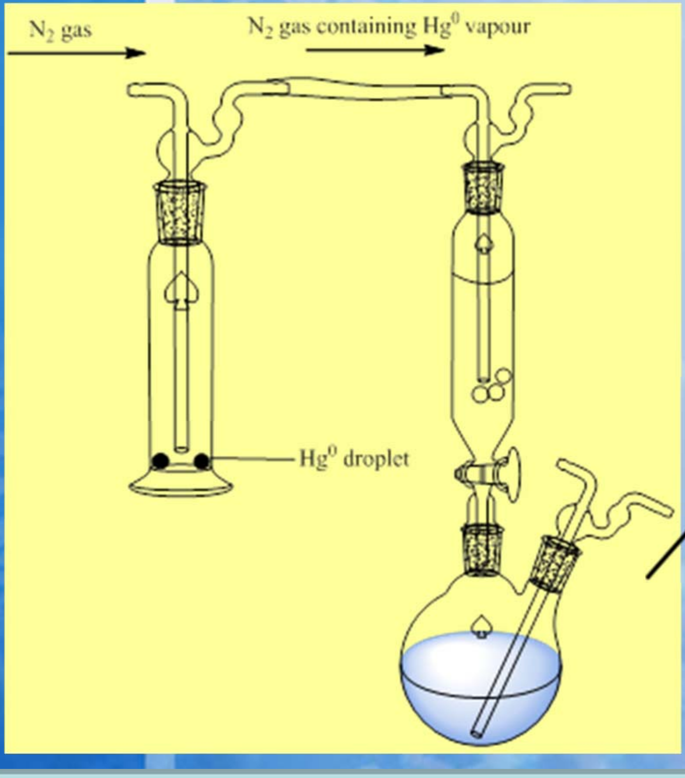
120 K

190 K

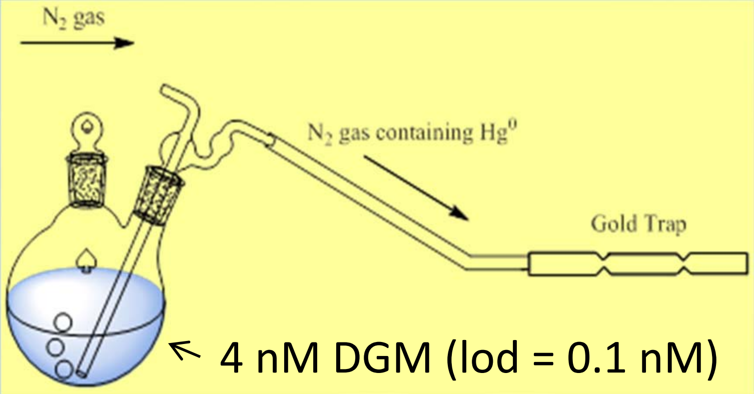
180 K

First spectroscopic observation that this type of oxidation process can occur in a frozen water-ice solid

# Dark oxidation of dissolved gaseous mercury (DGM) in ice



No chemical change with $Hg^{(0)}$ vapour in water-ice alone

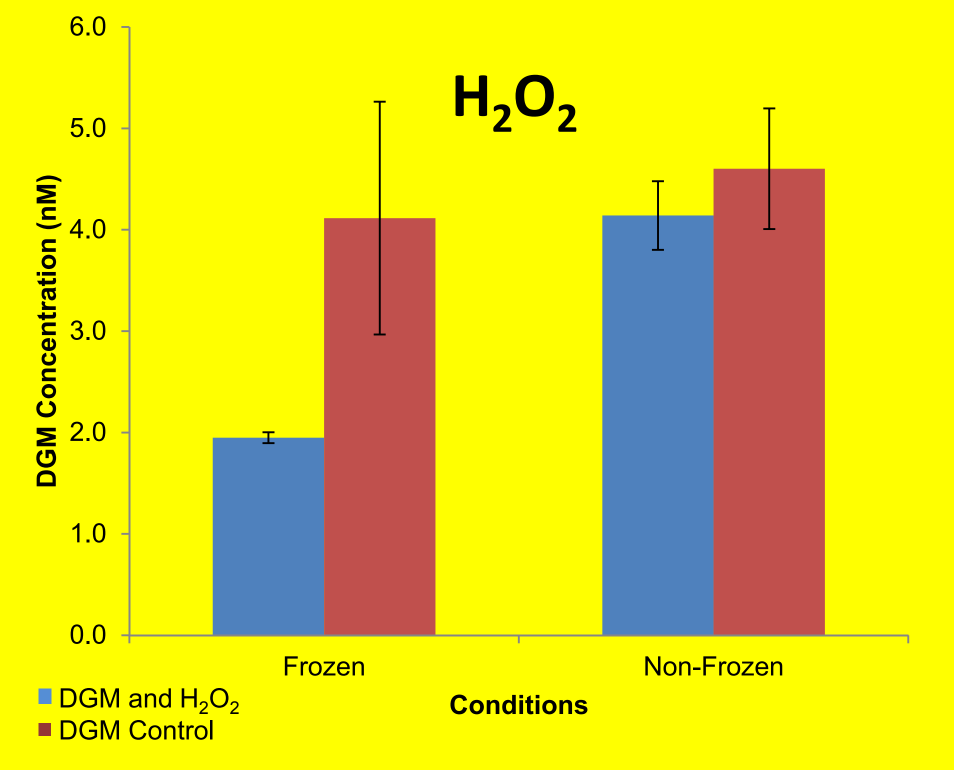


4 nM DGM (lod = 0.1 nM)

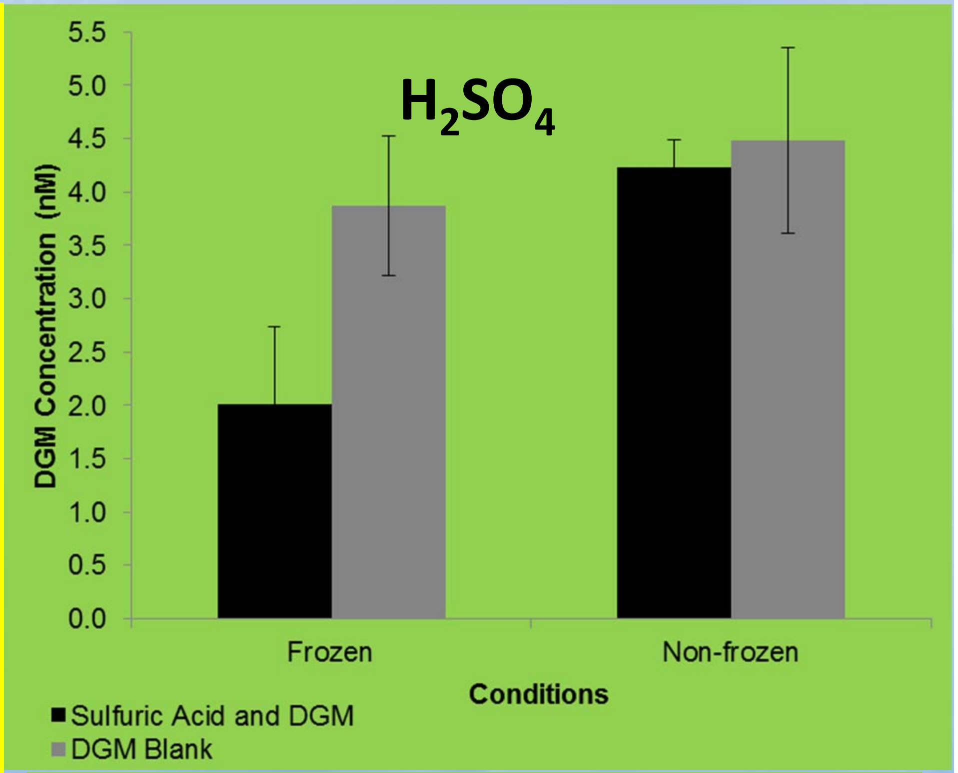
**Sir Galahad Cold Vapour Atomic Fluorescence Mercury Analyser**

- $N_2$ blown over Hg droplet and into deionised water (DGM solution).
- DGM solution added to flasks containing reagents.
- Flasks frozen and thawed.
- $N_2$ blown through flask to degas $Hg^0$ and carry it onto a gold trap.
- Gold trap containing $Hg^0$ placed in analyser.

# Freezing Hg$^{(0)}$with oxidants: $H_2O_2$ and $H_2SO_4$



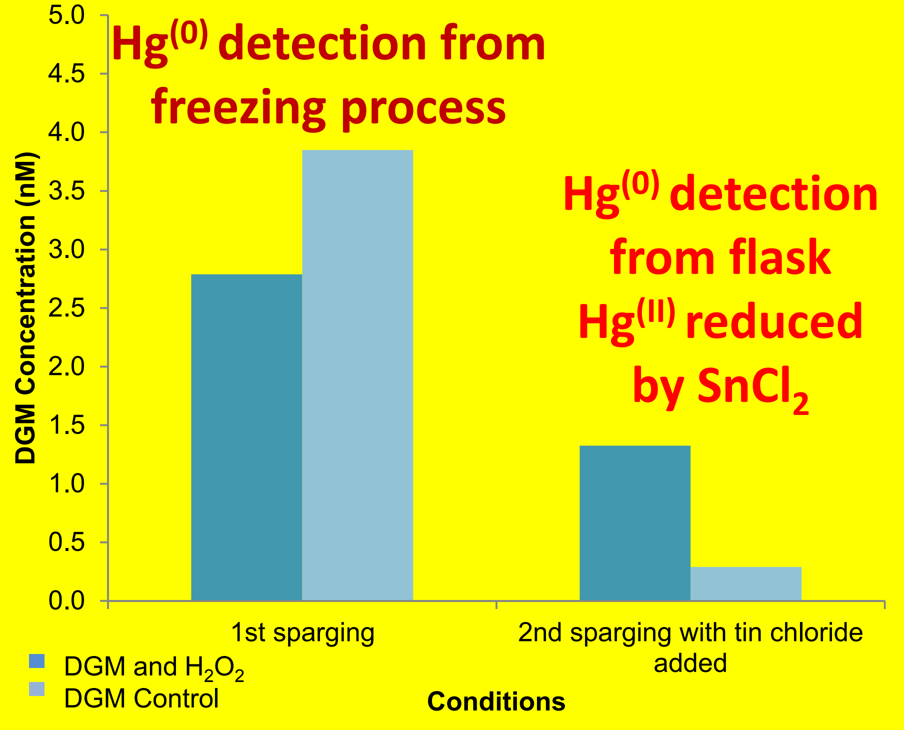
**Comparison of frozen and non-frozen solutions containing DGM and 0.44mM $H_2O_2$ with DGM controls**



**Comparison of frozen and non-frozen solutions containing DGM and $H_2SO_4$ (pH 2.5) with DGM controls**

- Freezing DGM in the presence of either $H_2O_2$ or sulfuric acid causes significant drops in DGM concentration. Six repeats for each sample. Proof of principle.
- No significant drop in DGM of non-frozen or control flasks. Six repeats for each sample
- Is drop in DGM is due to oxidation of Hg$^0$ to Hg$^{(II)}$? What remains in the flask?

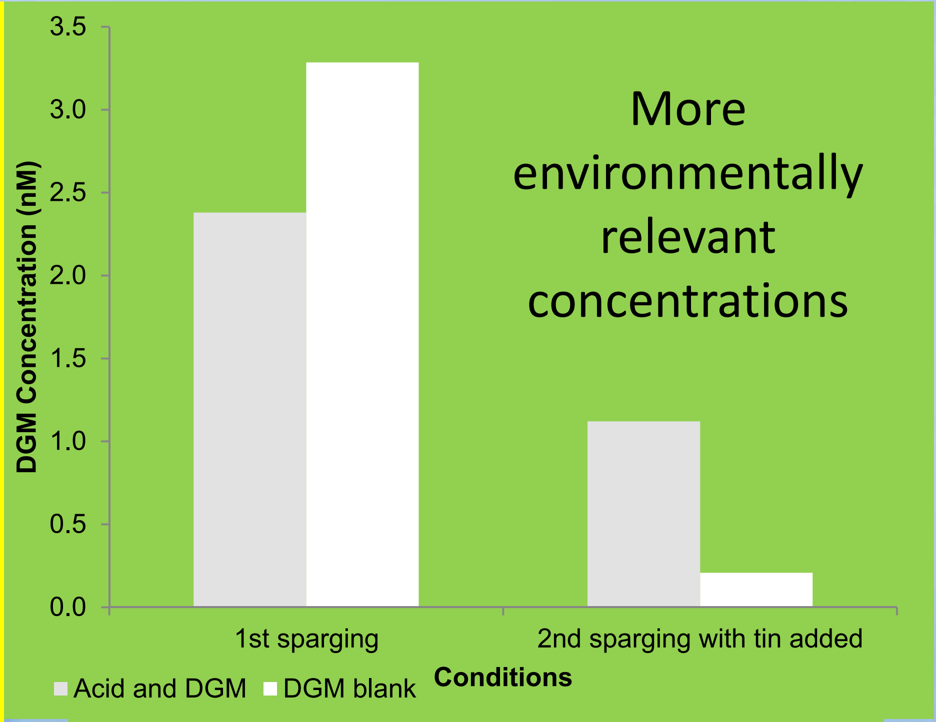
# $Hg^{(0)}$ “Froz-oxidation” to $Hg^{(II)}$: (Using Tin Chloride as a reducing agent)



**$Hg^{(0)}$ detection from freezing process**

**$Hg^{(0)}$ detection from flask $Hg^{(II)}$ reduced by $SnCl_2$**

**Addition of $SnCl_2$ to flasks containing DGM and 2.2 µM $H_2O_2$ following initial degassing of $Hg^0$.**



More environmentally relevant concentrations

**Addition of $SnCl_2$ to flasks containing DGM and sulfuric acid (pH 4.5) following initial degassing of $Hg^0$.**

- First sparging following the freezing process shows $Hg^0$ in flasks.
- Tin chloride (50 µM) then added to flasks in order to reduce any $Hg^{2+}$ present to $Hg^0$.
- Second degassing then recovers the $Hg^0$ which was reduced.
- Substantial DGM concentration recovered from flasks containing reagents which gives evidence for the oxidation of $Hg^0$ in frozen solutions.

# New pathways on ice explored!

**John Sodeau**
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**University College Cork**

3rd workshop on Air-Ice Chemical Interactions (AICI):
New York, USA. June 2011