Organic gas incorporation in ice studied by inelastic Raman scattering and X-ray diffraction

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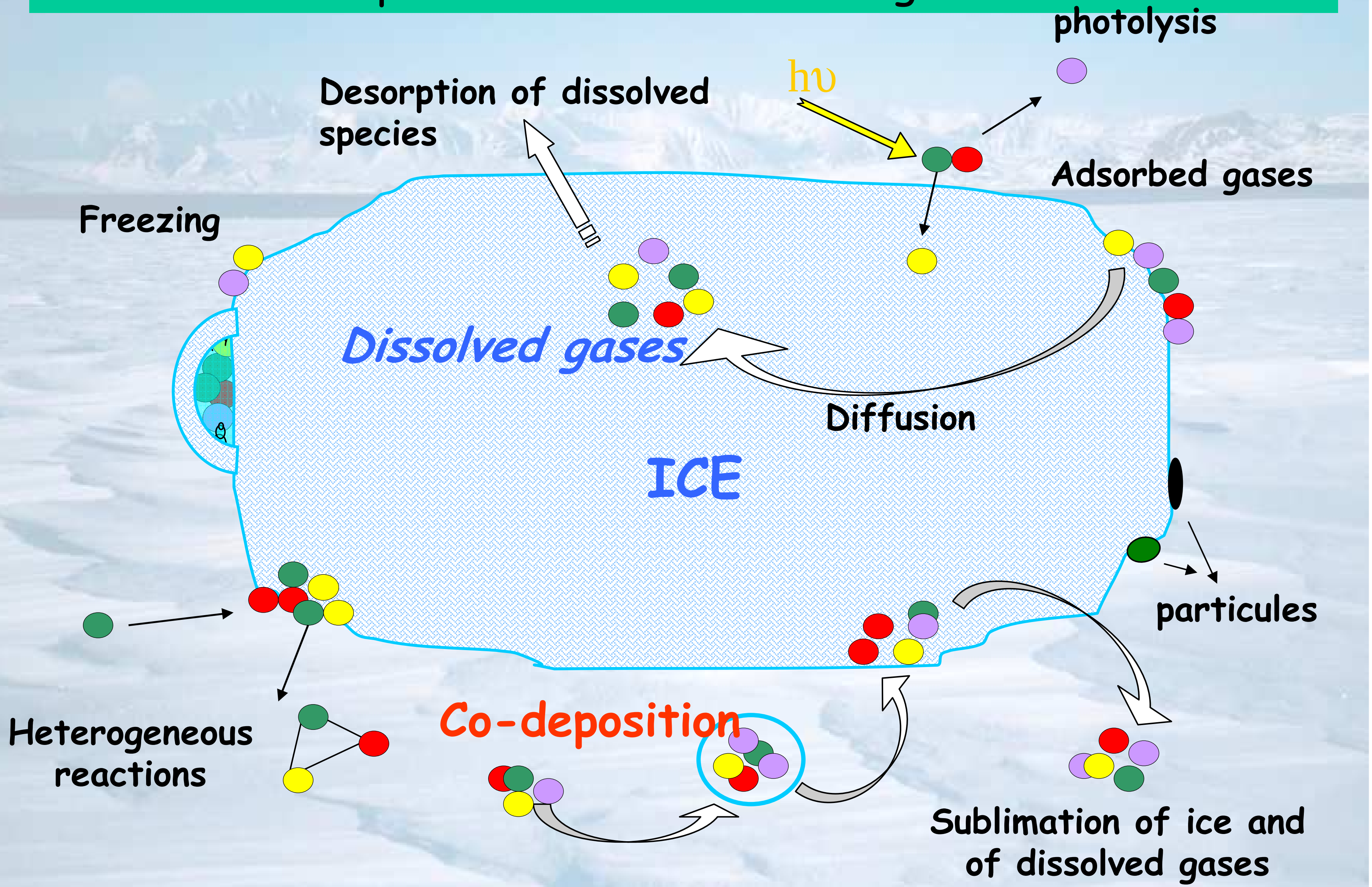
Different incorporation mechanisms at gas-water interface



Atmospheric chemistry implications

-Stratosphere: acids (HNO3, HCl, etc) interact strongly with surfaces of ice particles (PSC clouds): formation of various hydrates, heterogeneous reactions → Ozone destruction during winter in polar stratosphere

-Troposphere:

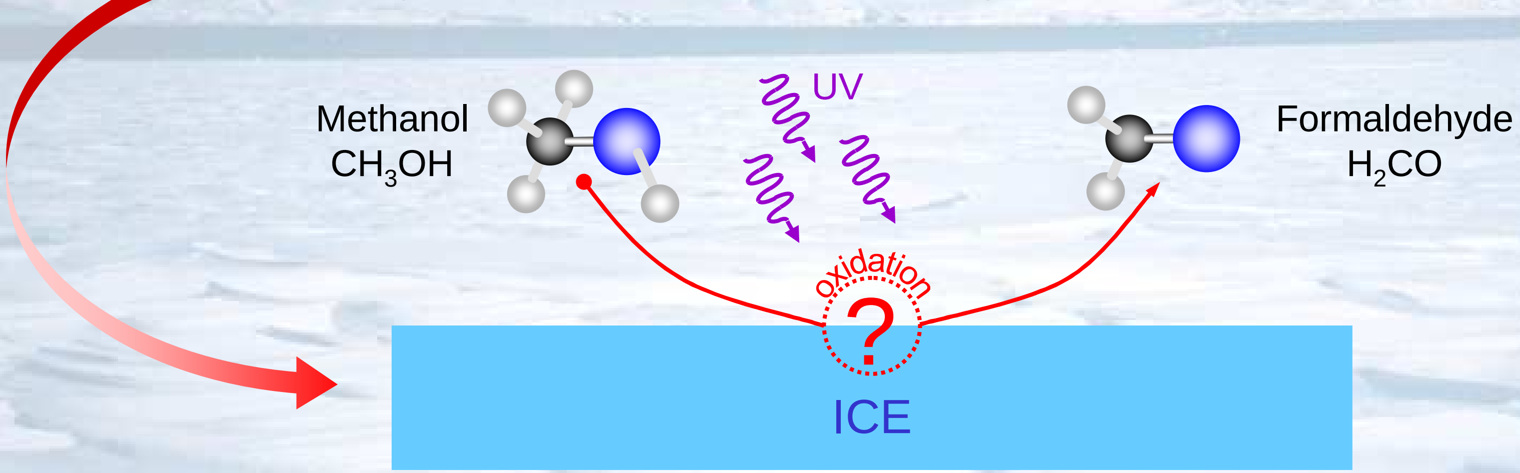
-ice particles in cirrus clouds (cover 30% Earth's surface) and ice from snowpack

-Presence of Volatile Organic Compounds (VOC) in Troposphere (Singh et al., Nature (2001). Interaction of VOC with ice ?

--> Adsorption on ice (ΔHads ~ -60 kJ/mol), Sokolov & Abbatt JPC A (2002), Winkler et al., PCCP (2002), Peybernès et al., JPC B (2004) consistent with H-Bonds formation (strength ~ 20 kJ/mol) with water molecules at the surface

- **In upper troposhere** : correlation between high H_2CO and CH_3OH concentration (*Jaegle et al.*, J. Geophys. Res. 105 (2000) 3877-3892)

Species	Concentration obs. (pptv) Gas phase	Model prediction (pptv) Gas phase	Ratio
H_2CO	~ 350	50	x 7



- **In snowpack**:

Species	Concentration Measured (pptv)	Model prediction Gas phase (pptv)	Ratio
H_2CO	200	70	x 3
CH_3CHO	80	40	x 2
NO_x	25	1	x 25
HONO	20	1	x 20

(A.L. Sumner *et al.*, Atmos. Environ. 36 (2002) 2553-2562 ; S. Perrier *et al.*, Atmos. Environ. 36 (2002) 2695-2705)

Needs for investigations of other incorporation mechanisms !

Astrophysics

- Close problematic of gas incorporation but at lower p and T !

-Interstellar medium : Ice possesses a high capacity for capture of gases (ex: H_2CO, CH_3OH etc…) and there exists possibility for ice to reject them in different temperature ranges (lower T° and P)

-Sequestration of gases by condensation have potential interest in order to understand the evolution and history of comets

→Importance to study how gaseous species are incorporated in ice
→Which structures it forms when incorporated

Objectives:

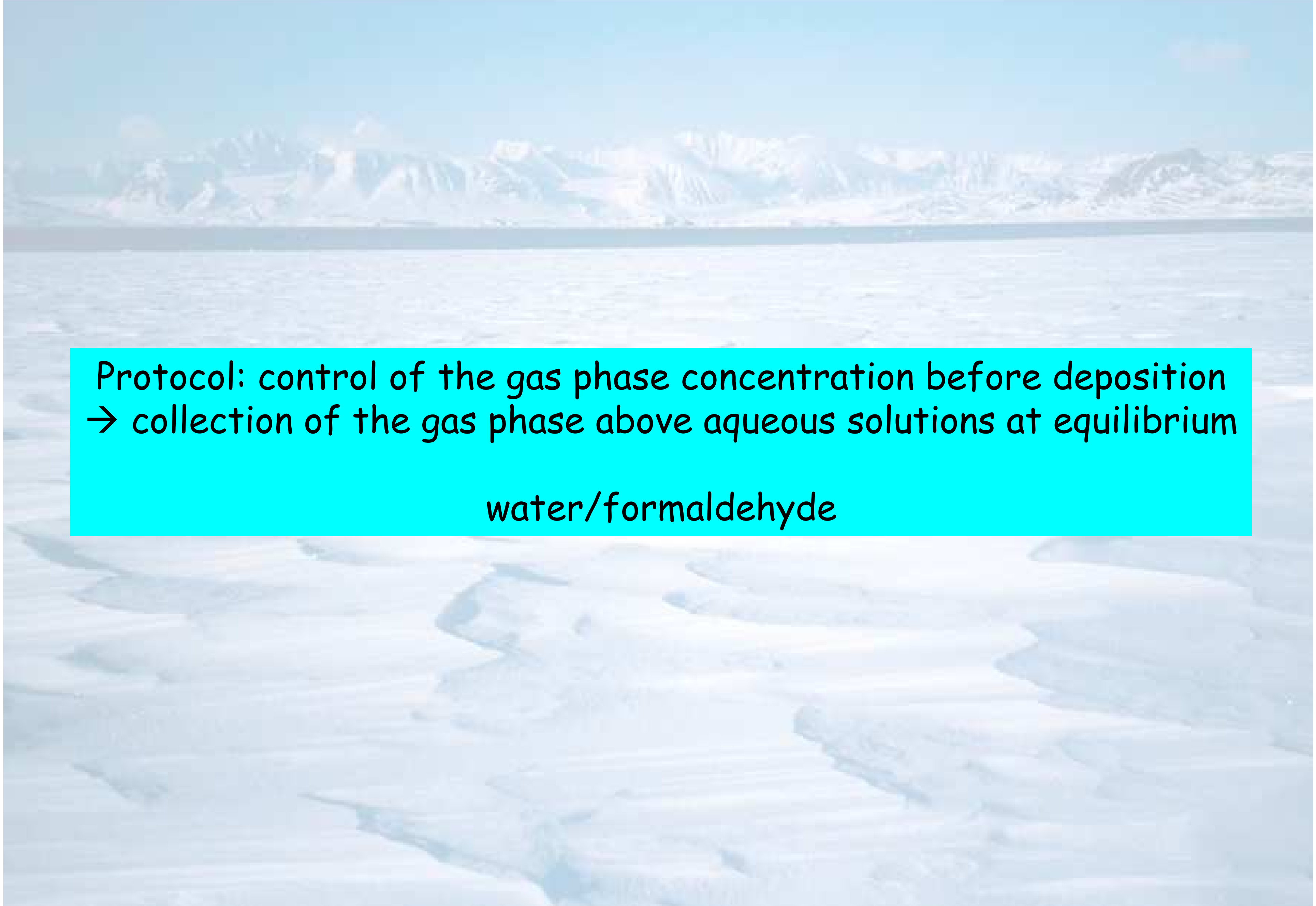
- Study the co-deposition of a VOC and water i.e. which structure it forms
- How gas and water partitioned in ice : concentration ?

↳

o Determination of the nature of the solid phases formed by co-condensation or separate condensation (crystalline, amorphous, hydrates, separated phases ect.,) by Raman spectroscopy, X-ray diffraction

o Determination of the [VOC]

o Attempt to answer more fundamental questions concerning gas-ice interactions in condensed thin films

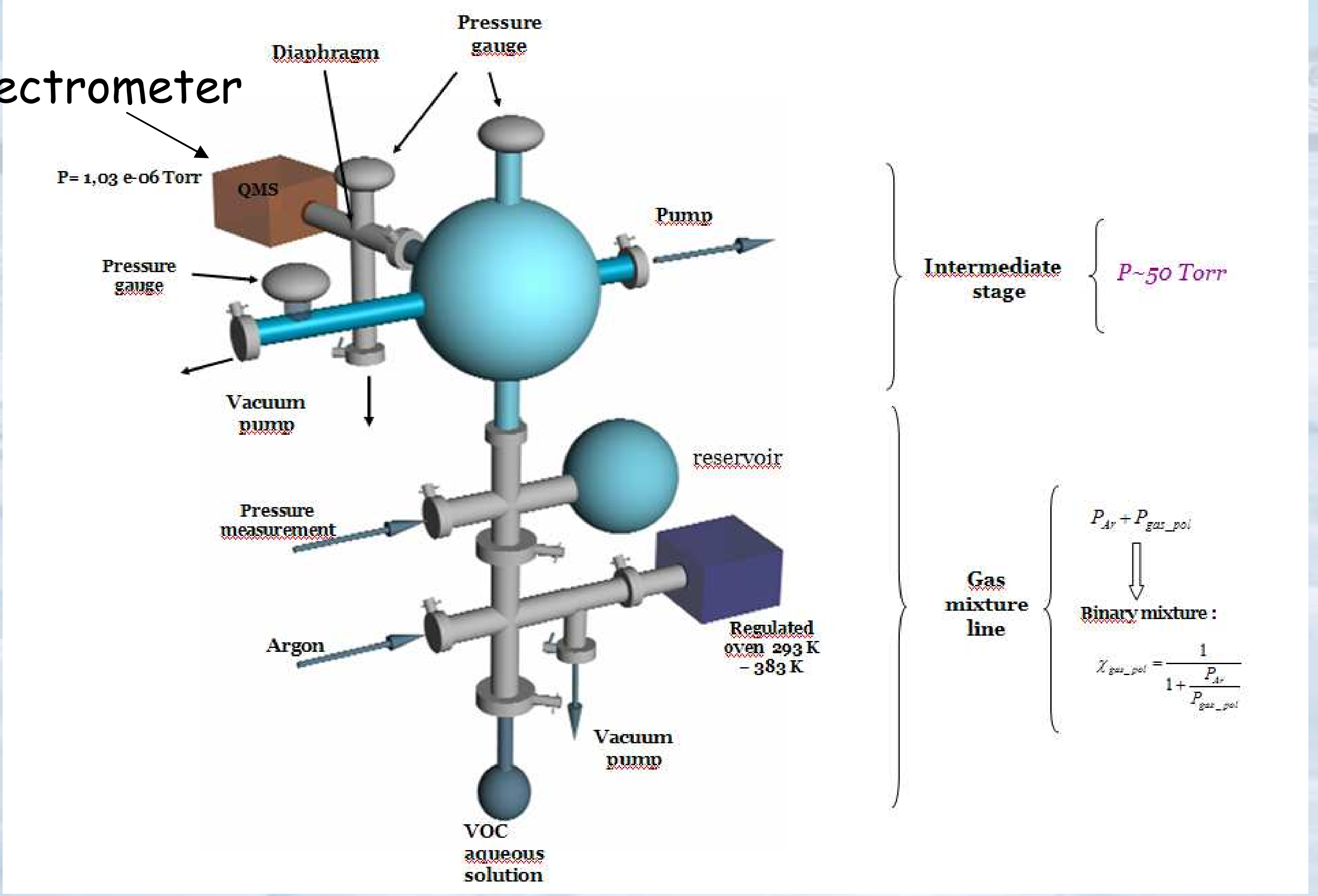


Protocol: control of the gas phase concentration before deposition
→ collection of the gas phase above aqueous solutions at equilibrium

water/formaldehyde

Experimental set-up developed for quantitative gas phase analysis

Mass spectrometer

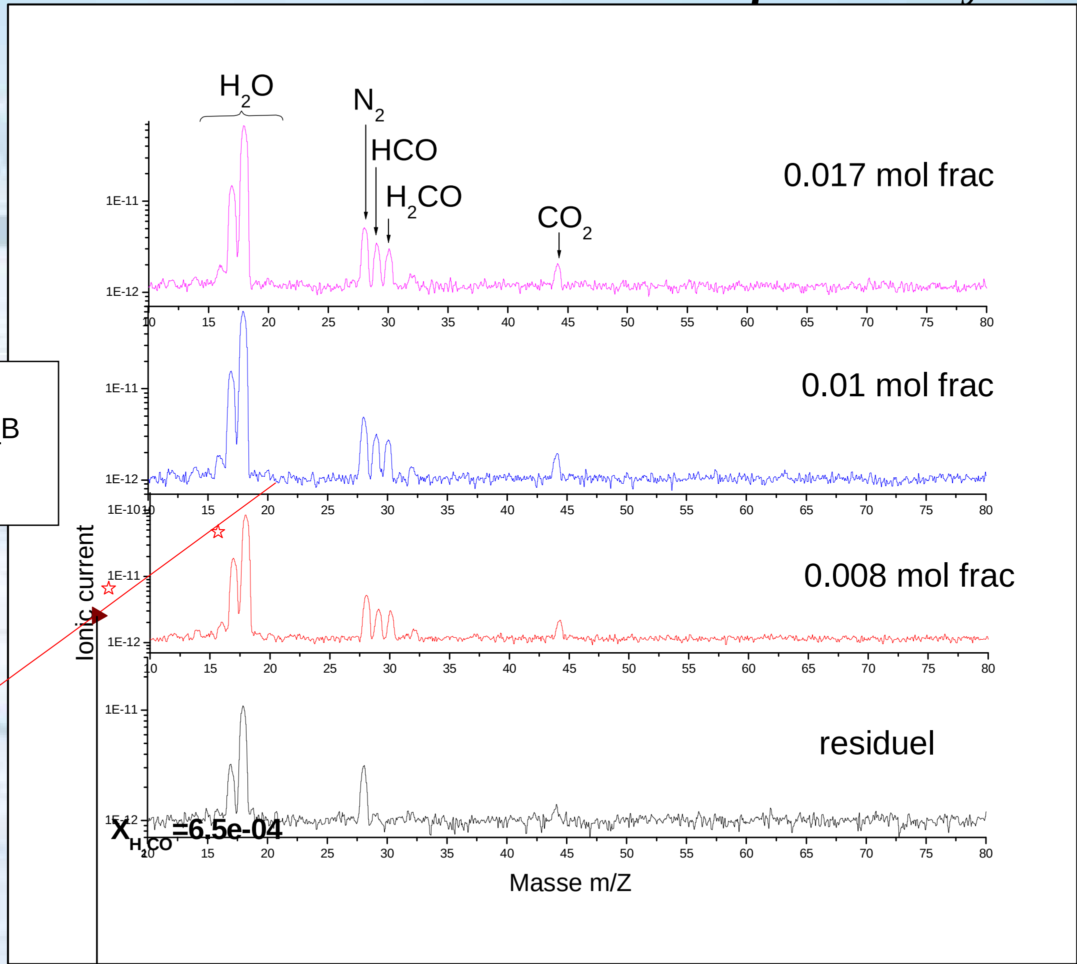


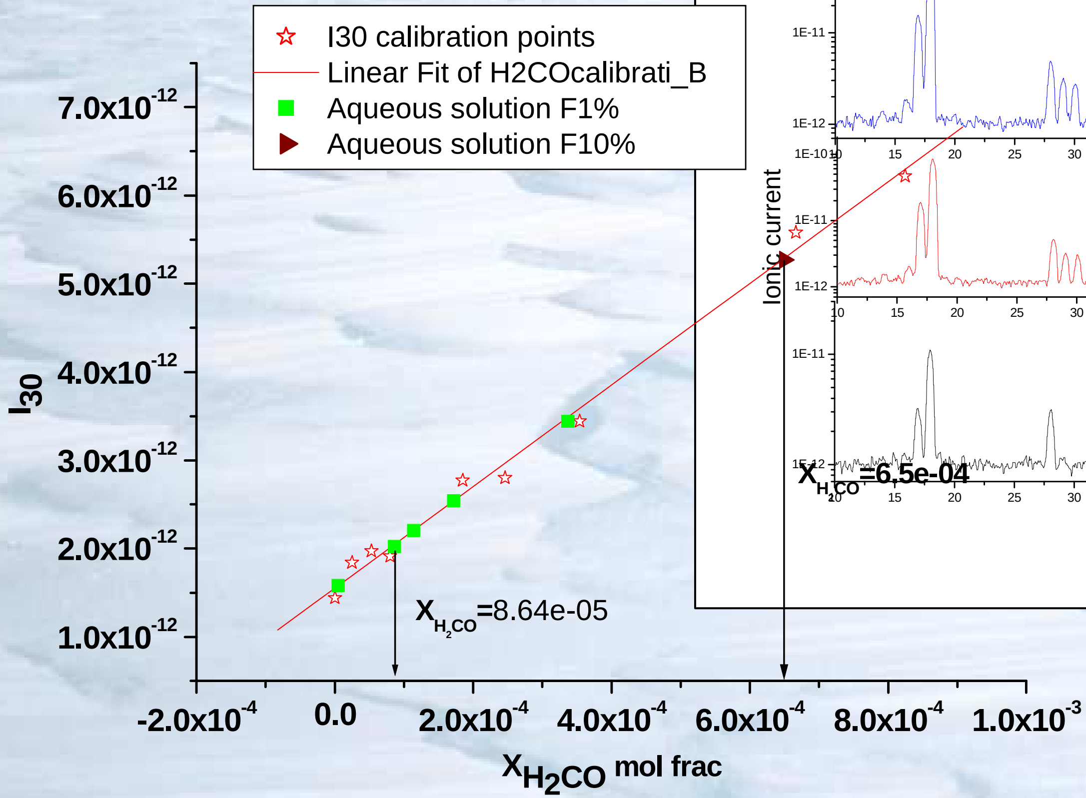
Gas collected above aqueous solutions of H_2O:H_2CO

Mass spectrometry

Gas Phase: H_2O+ H_2CO

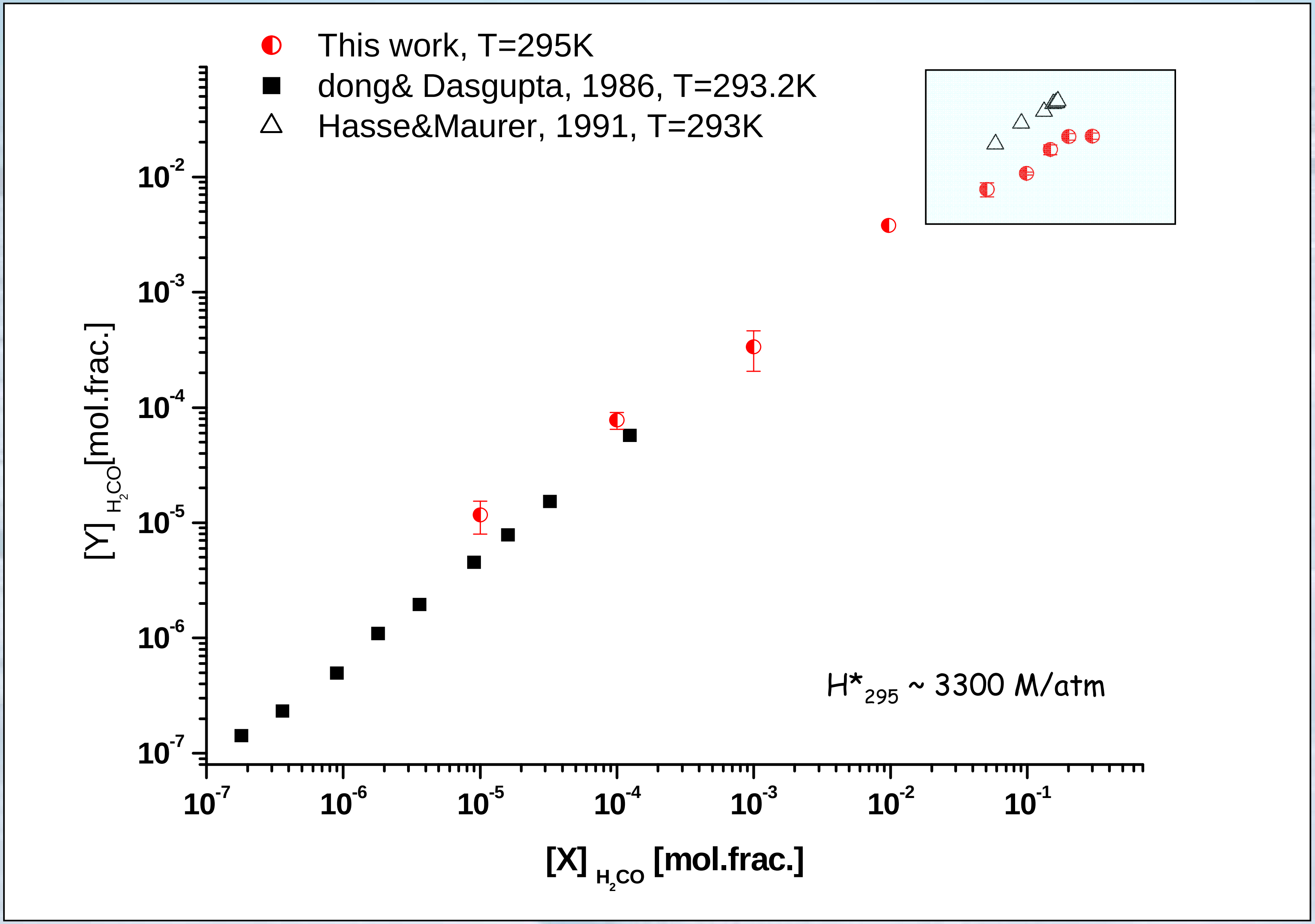
Liquide Phase:
oligomers ($HO(H_2CO)_nH$)





M_{48} ($HOCH_2OH$) absent

Cross calibration using Mass Spectrometry and IR absorption technics



Composition of H_2CO-H_2O gas mixtures collected above aqueous solutions

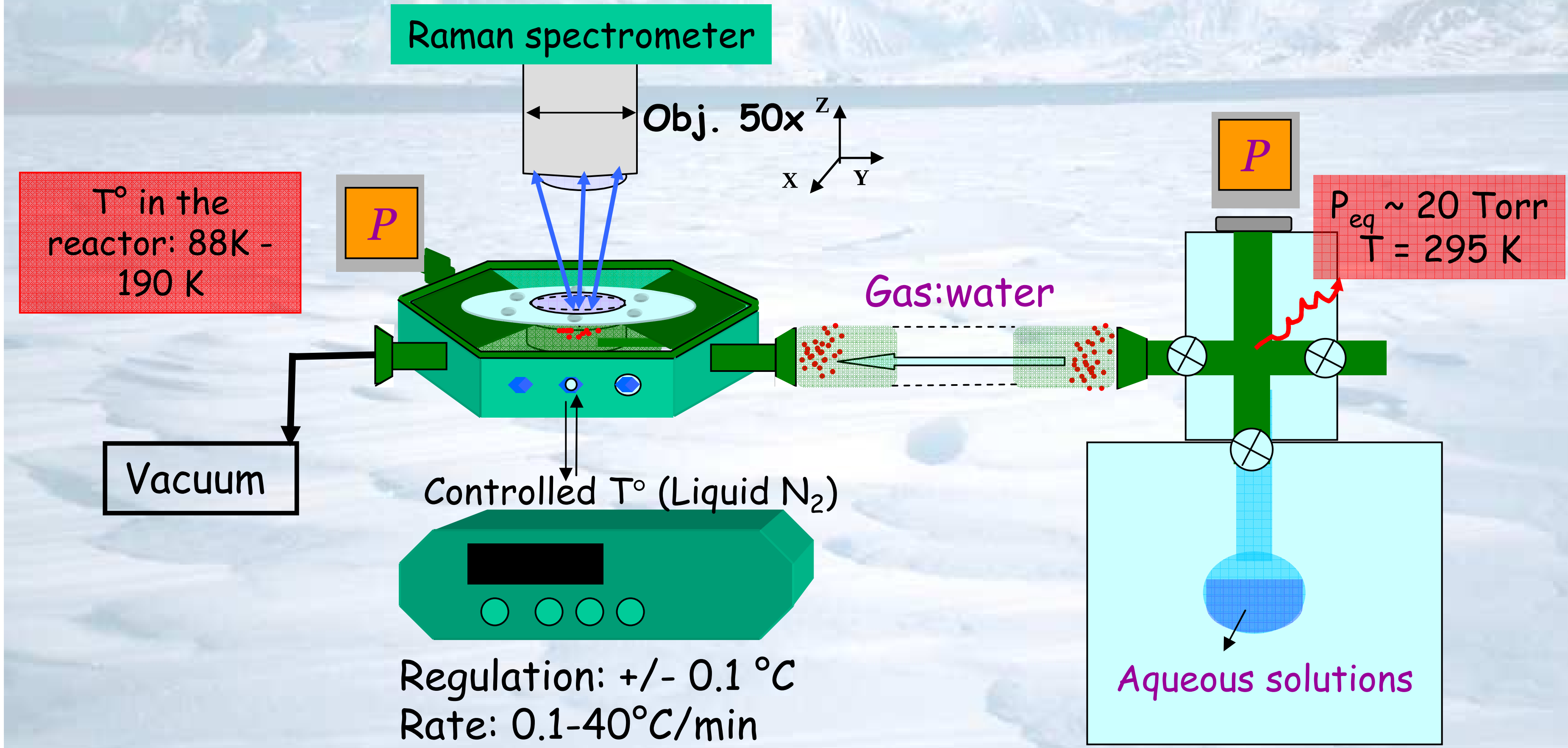
χ_{H_2CO} (solutions aqueuses) mol%	$P_{H_2O} : P_{H_2CO}$ **Gas**	**Gas phase mol% obs.** χ_{H_2CO}	**Solide phase mol% (calc.)** χ_{H_2CO}
1	262:1	**0.38**	**0.3**
5	127:1	**0.8**	**0.6**
10	92.1	**1.1**	**0.8**
15	57:1	**1.7**	**1.3**
20	62:1	**1.6**	**1.3**
30	43:1	**2.3**	**1.7**

$$P_{H_2CO} = \chi_{gaz} * P_{tot}$$ Gas phase

$$\chi_{H_2CO} = \frac{1}{1 + \frac{P_{H_2O}}{P_{H_2CO}} \frac{\alpha_{H_2O}}{\alpha_{H_2CO}} \sqrt{\frac{M_{H_2CO}}{M_{H_2O}}}}$$ Solide phase

Dominé & Thibert, *Geophys. Res. Lett.* 1996

Experimental protocol



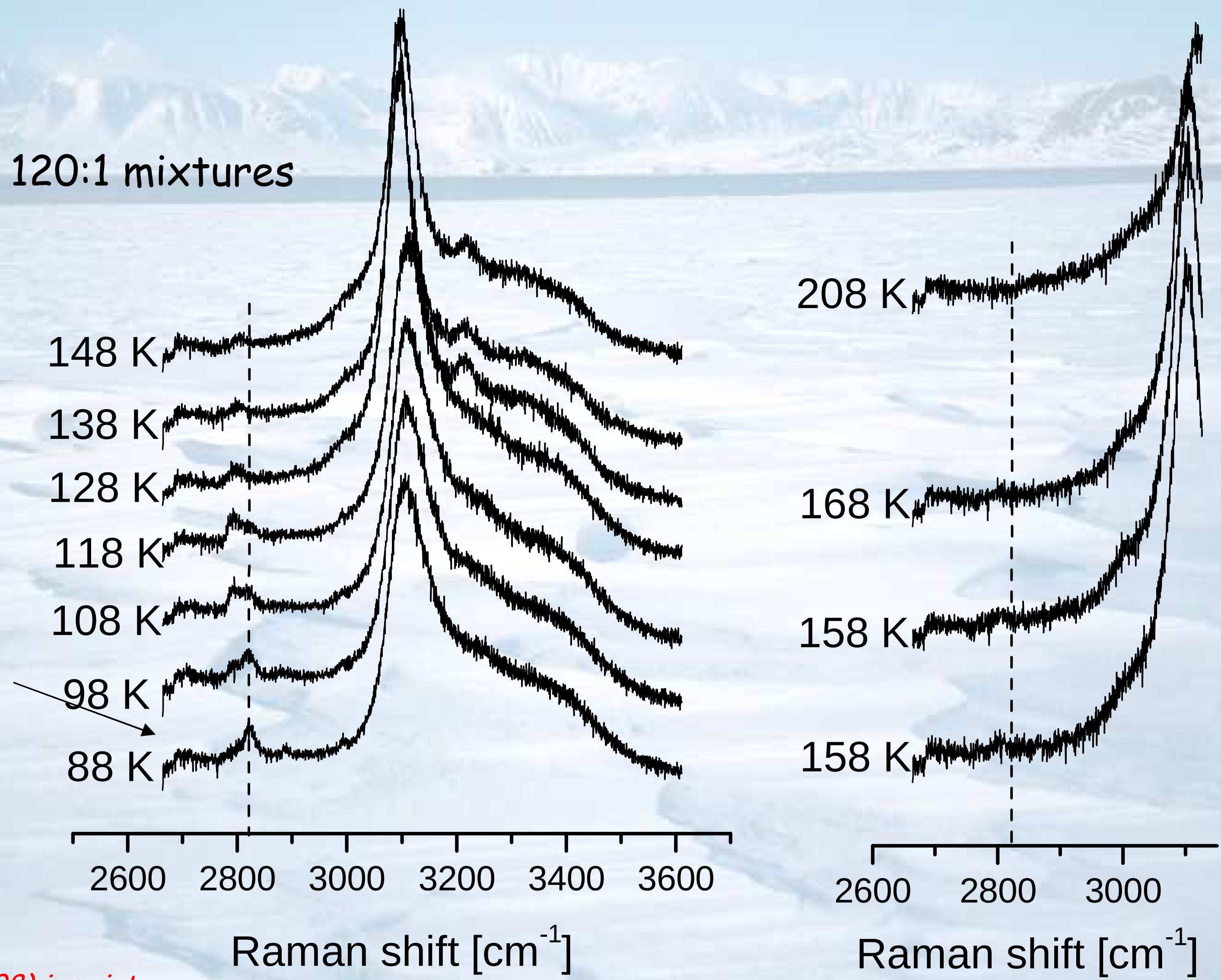
Regulation: +/- 0.1 °C
Rate: 0.1-40°C/min

Ice film thickness: ~ 170 μm

Temperature evolution of the ice film under vacuum

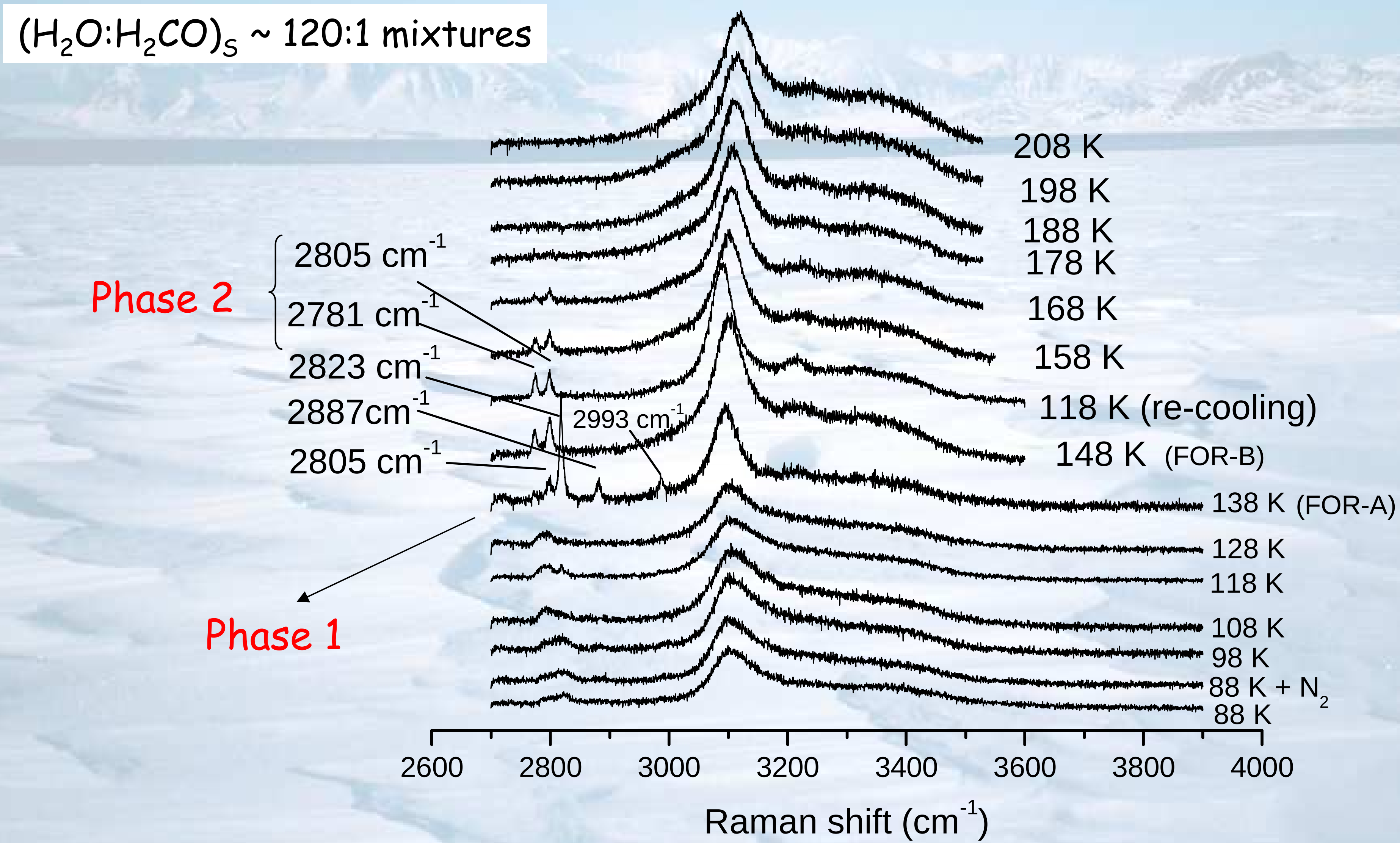
$(H_2O:H_2CO)_S$ ~ 120:1 mixtures

C-H stretch of H_2CO distributed molecularly in ASW

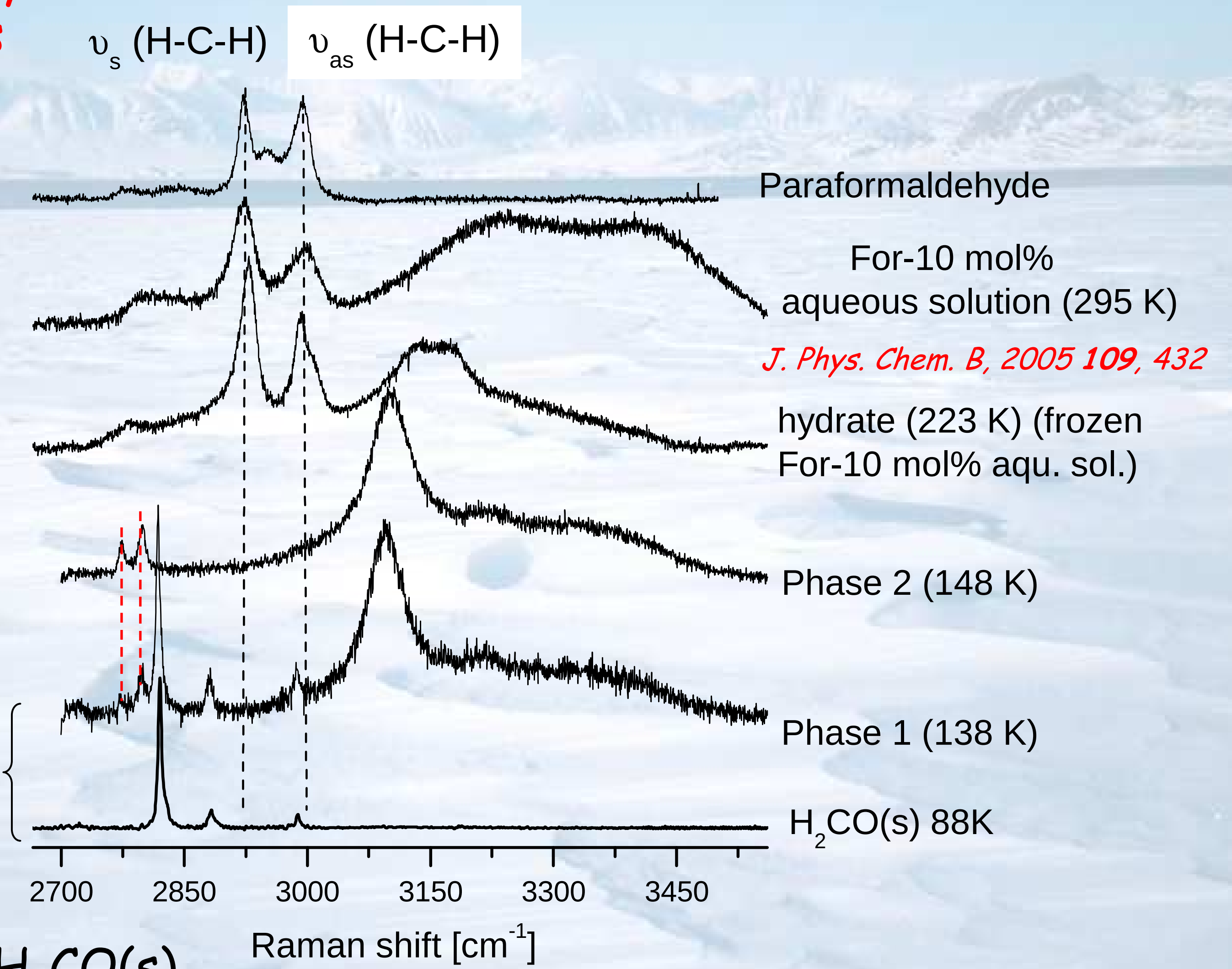


Chazallon et al. PCCP (2008) in print

Temperature evolution of the film under N_2 atmosphere



Molecular spectra of different formaldehyde based compounds



Mixed phase 1 + 2

Phase 1 = $H_2CO(s)$

Ripmeester et al. J. Phys. Chem.1996

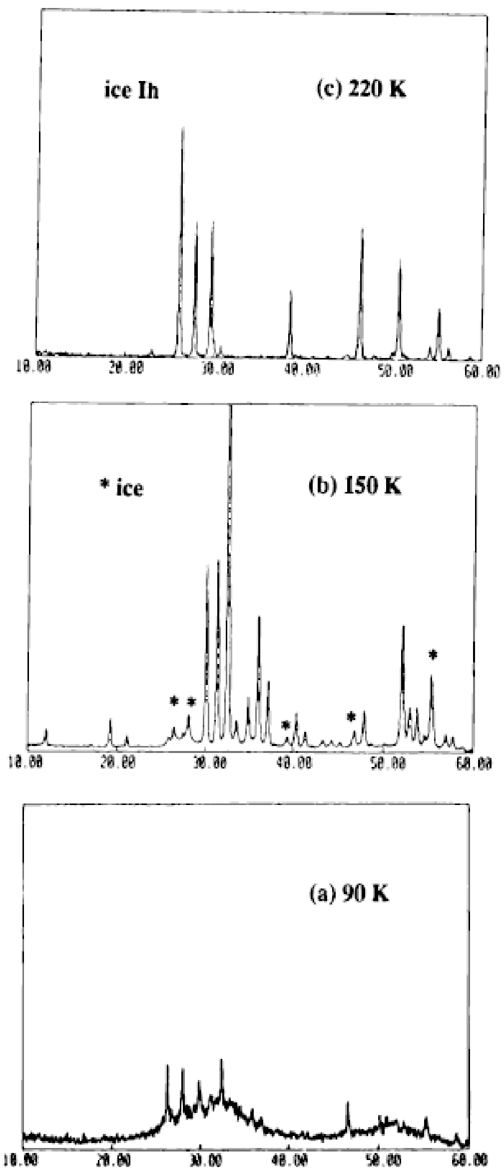
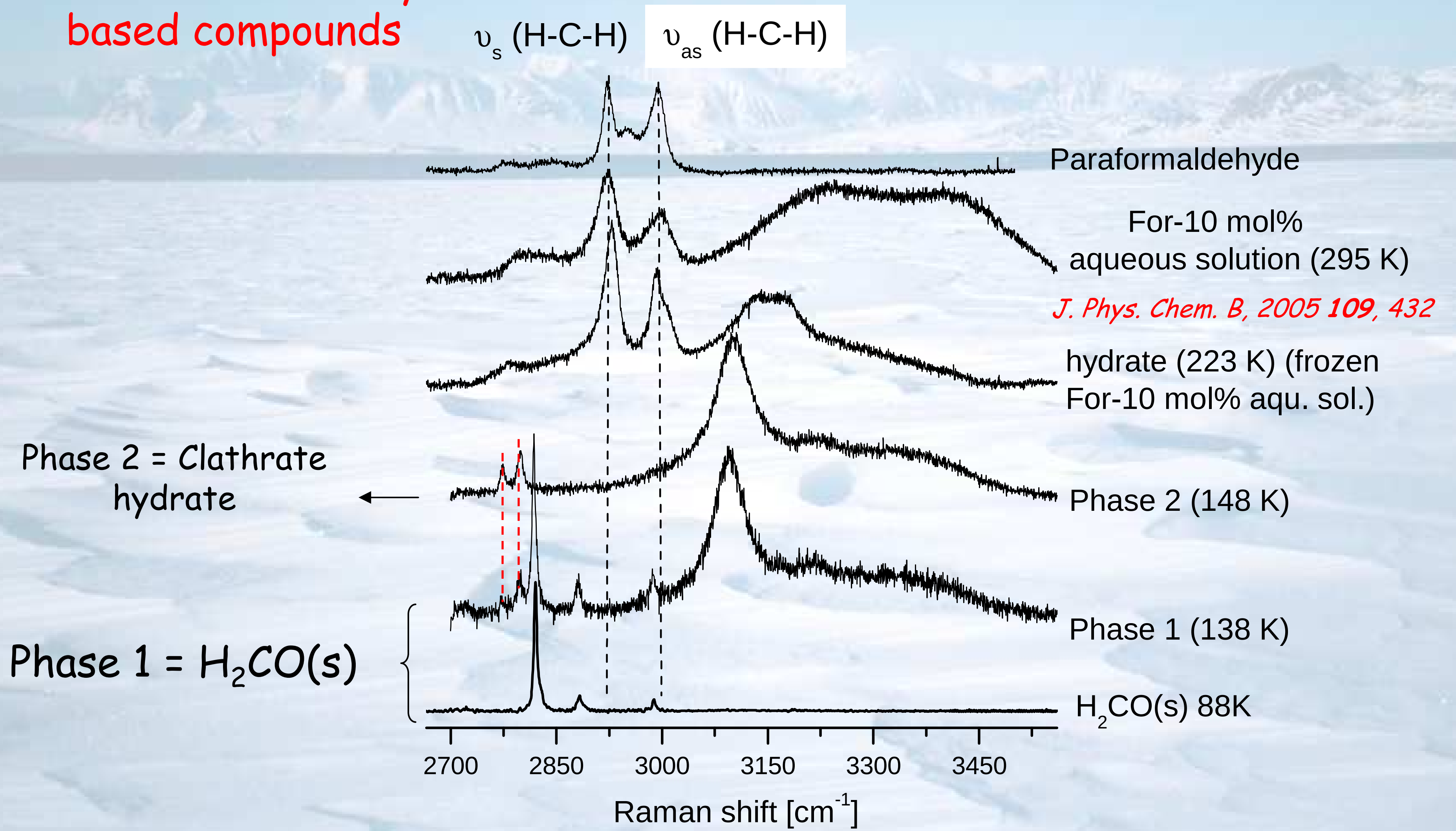


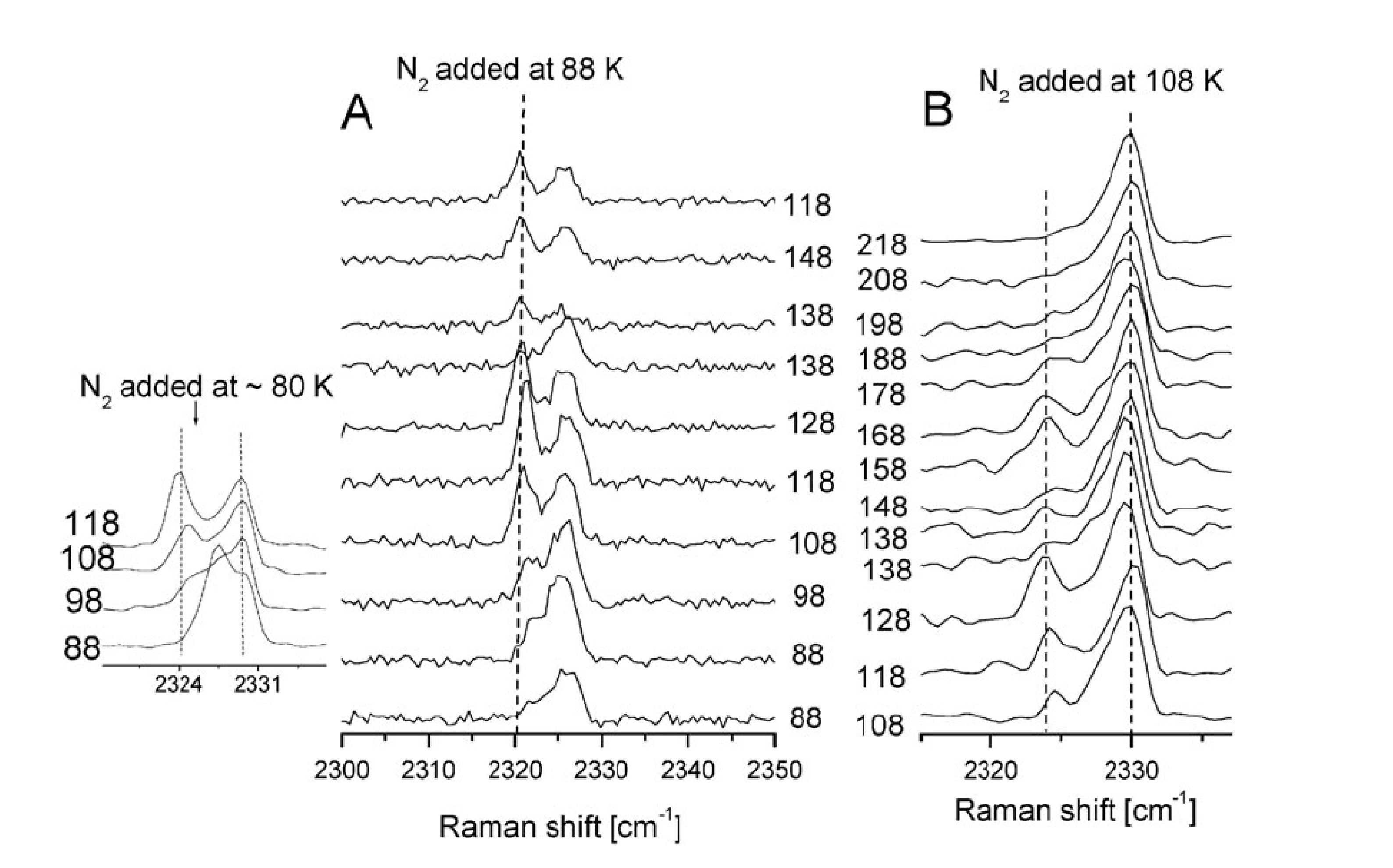
Figure 1. X-ray powder diffraction pattern of (a) a vapor deposit of water vapor and formaldehyde gas prepared from a paraformaldehyde precursor at 90 K; (b) after annealing at 150 K; (c) after annealing at 220 K.

→ Ice + type I H_2CO-hydrate

Molecular spectra of different formaldehyde based compounds



N_2 stretching mode spectral region



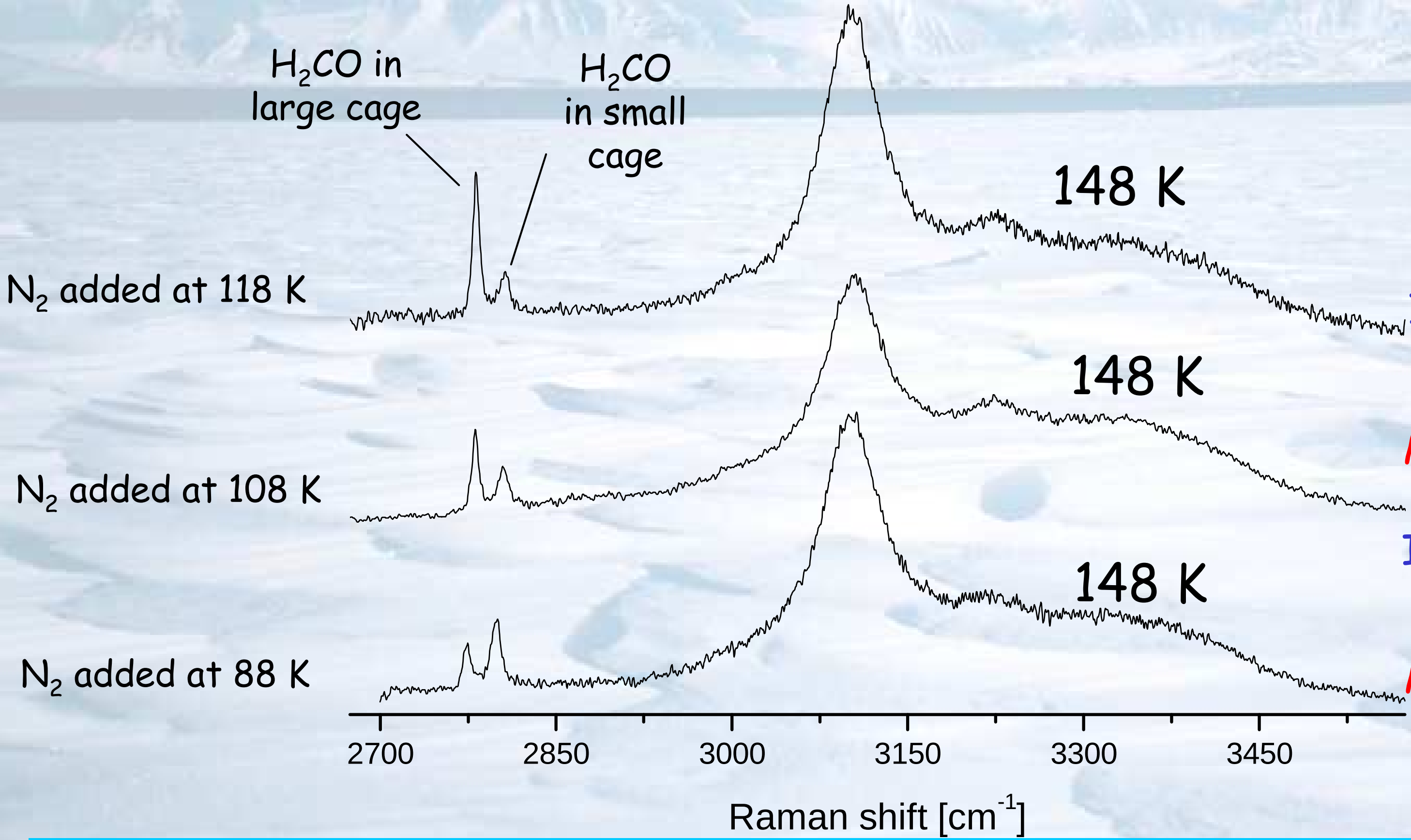
Discrimination between different hydrate structures

Raman intensity:

$I \; \alpha \; I_0 \, N_i \, \sigma_r \, f$

Ideally $I_{LC} / I_{SC} = 0.33$ → Type I

Ideally $I_{LC} / I_{SC} = 2$ → Type II



H$_2$CO hydrate type I
$I_{2805}/I_{2781} \sim 0.35$

Mixed N$_2$-H$_2$CO hydrate type I
$I_{2805}/I_{2781} \sim 0.7$

Mixed N$_2$-H$_2$CO-hydrate type II
$I_{2805}/I_{2781} \sim 1.6$

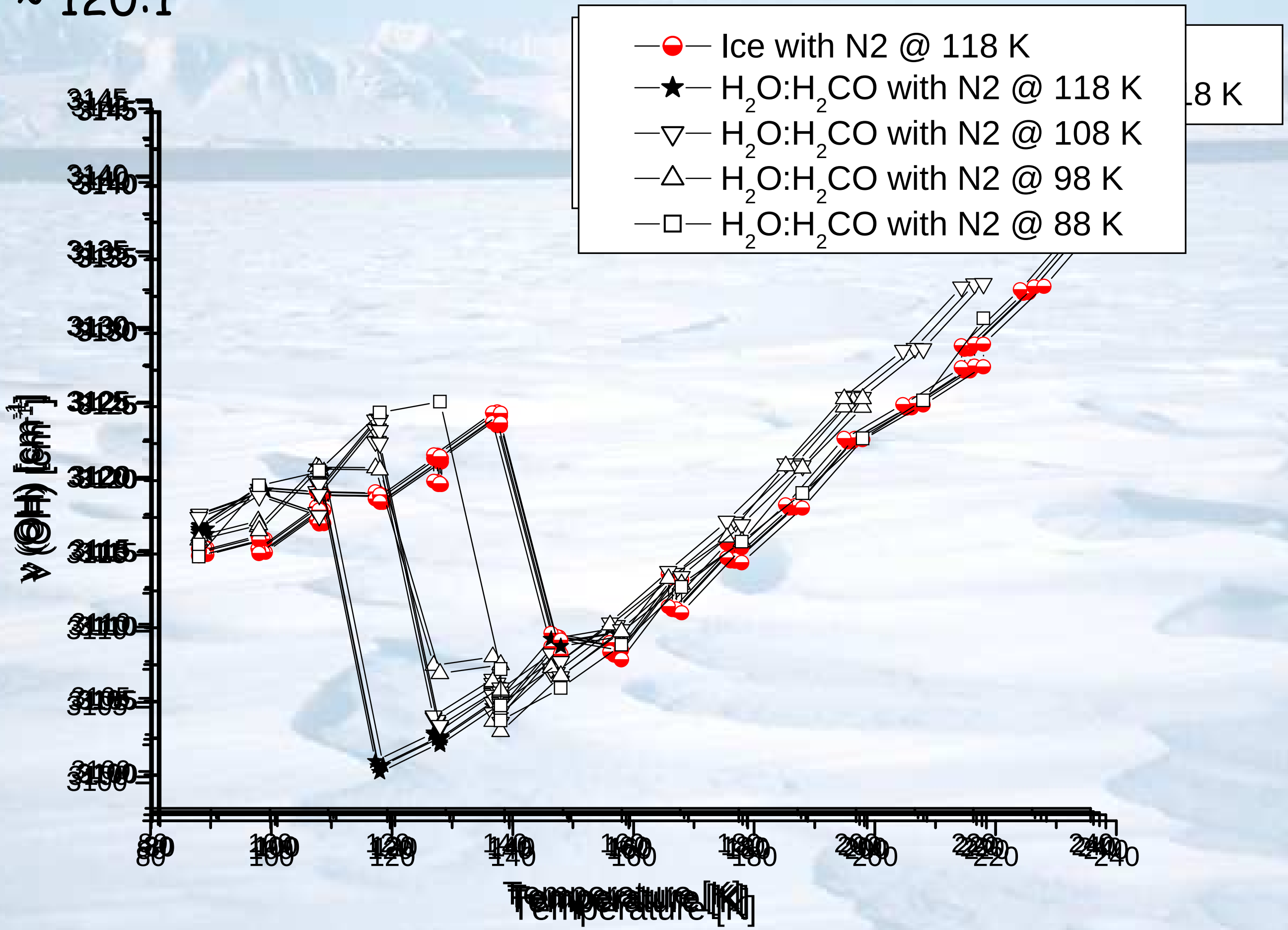
N_2 is sII former whereas H_2CO is sI hydrate former

Phase 2 is sI or sII depending on the relative N_2/H_2CO in the co-deposit

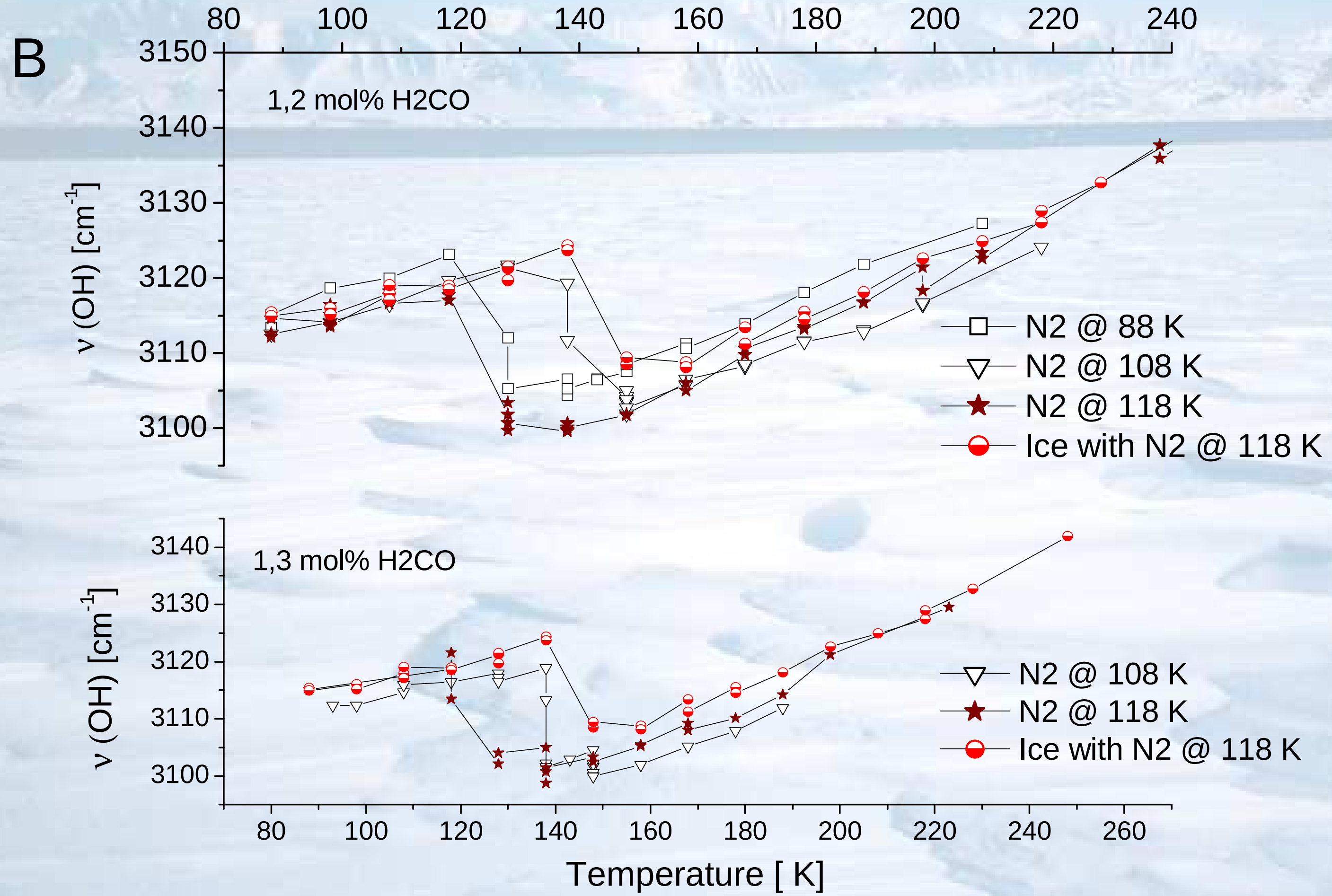
Competition between N_2 and H_2CO for the occupation of small cages -> type II formation

Crystallization of ice influenced by occlusion of gaseous N_2 and H_2CO

$(H_2O:H_2CO)_S \sim 120:1$



Only H_2CO in the co-deposit → ice Ic crystallization T° reduces
N_2/H_2CO increases → ice Ic crystallization T° increases


B
1,2 mol% H2CO
ν (OH) [cm-1]
N2 @ 88 K
N2 @ 108 K
N2 @ 118 K
Ice with N2 @ 118 K
1,3 mol% H2CO
ν (OH) [cm-1]
N2 @ 108 K
N2 @ 118 K
Ice with N2 @ 118 K
Temperature [K]

Co-deposition Ethanol/H_2O

❖ Vapor Liquid Equilibrium (VLE) data at 295 K: Ethanol/Water

Non-ideal solution
Ethanol:water

Gas Phase (Wilson model)

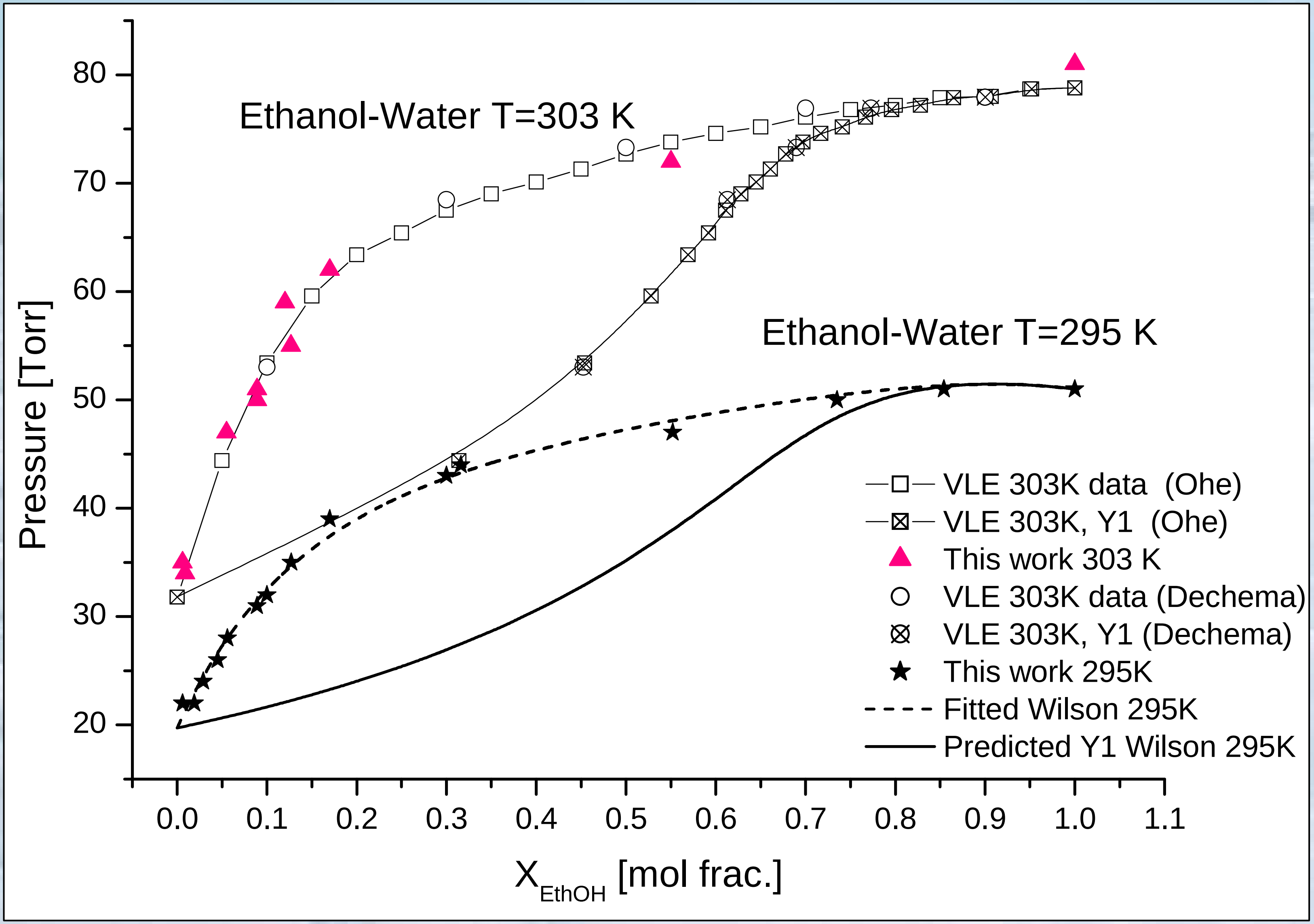
$$Y_{EtOH} = \frac{P_{EtOH}\gamma_{EtOH}X_{EtOH}}{P}$$

Condensed phase

$$X_{Eth} = \left(1 + \frac{P_{H2O}\alpha_{H2O}\sqrt{M_{Eth}}}{P_{Eth}\alpha_{Eth}\sqrt{M_{H2O}}}\right)^{-1}$$

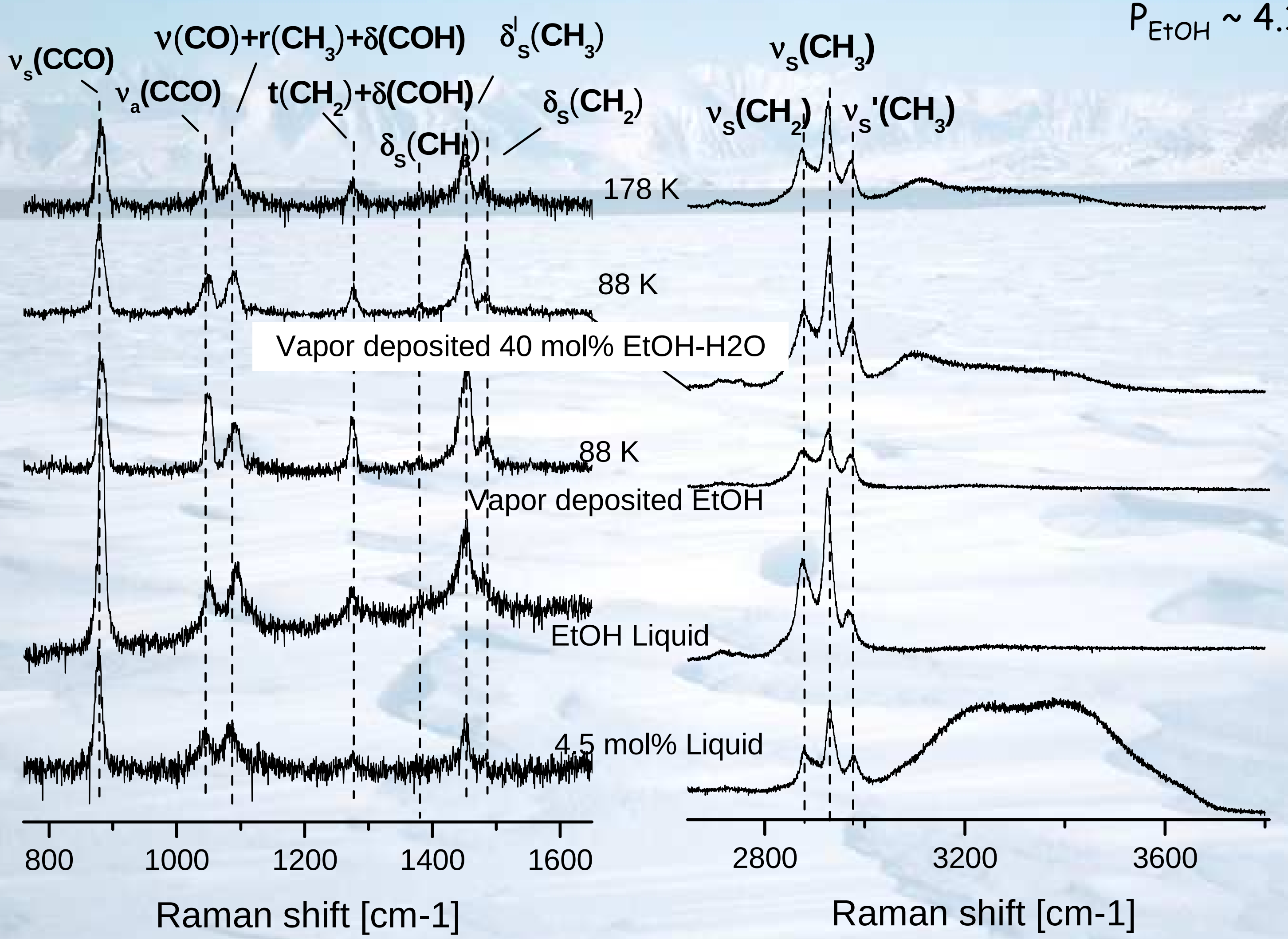
Dominé & Thibert, *Geophys. Res. Lett.* 1996

Xeth (LIQUID) Mol%	YEth (GAS) Mol%	$P_{EtOH}:P_{H2O}$ (GAS)	Xeth (SOLID) Mol%
0.6[a]	5.8	1:16	3.7[a]
1	9.2	1:9.9	5.9
1.9[a]	15.7	1 :5.4	10.4[a]
2.9	21.7	1 :3.6	14.8
4.5[a]	29.2	1 :2.4	20.5[a]
5.6	33.3	1 :2.0	23.7
8.9[a]	42.3	1 :1.4	31.4[a]
10	44.5	1 :1.2	33.4
12.7	49	1 :1.0	37.5
17[a]	54.2	1 :0.8	42.5[a]


Ethanol-Water T=303 K
Ethanol-Water T=295 K
Pressure [Torr]
80
70
60
50
40
30
20
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
X EthOH [mol frac.]
VLE 303K data (Ohe)
VLE 303K, Y1 (Ohe)
This work 303 K
VLE 303K data (Dechema)
VLE 303K, Y1 (Dechema)
This work 295K
Fitted Wilson 295K
Predicted Y1 Wilson 295K

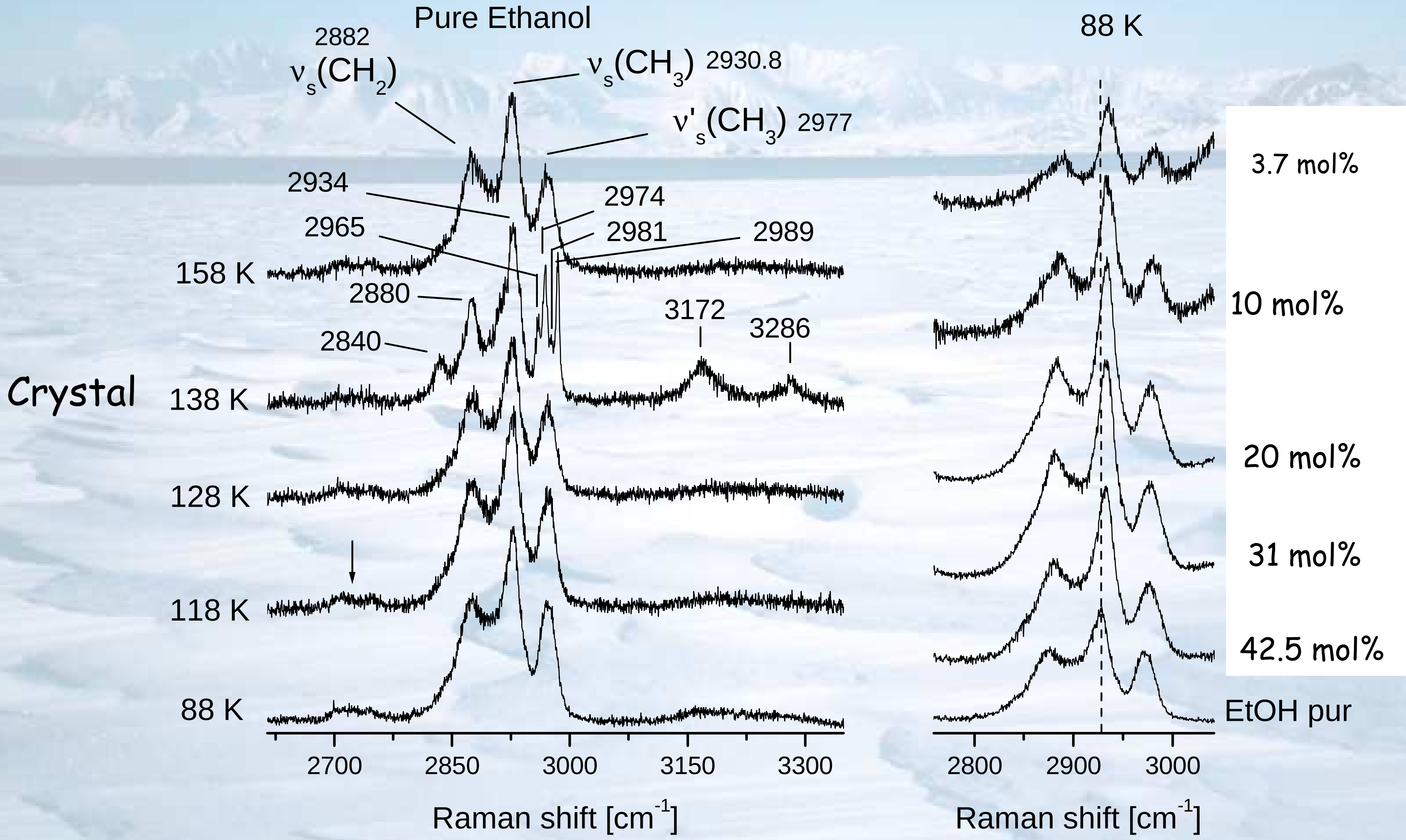
2. Comparative Raman analysis of co-deposits / aqueous solutions

$P_{EtOH} \sim 4.10^{-2}$ Torr



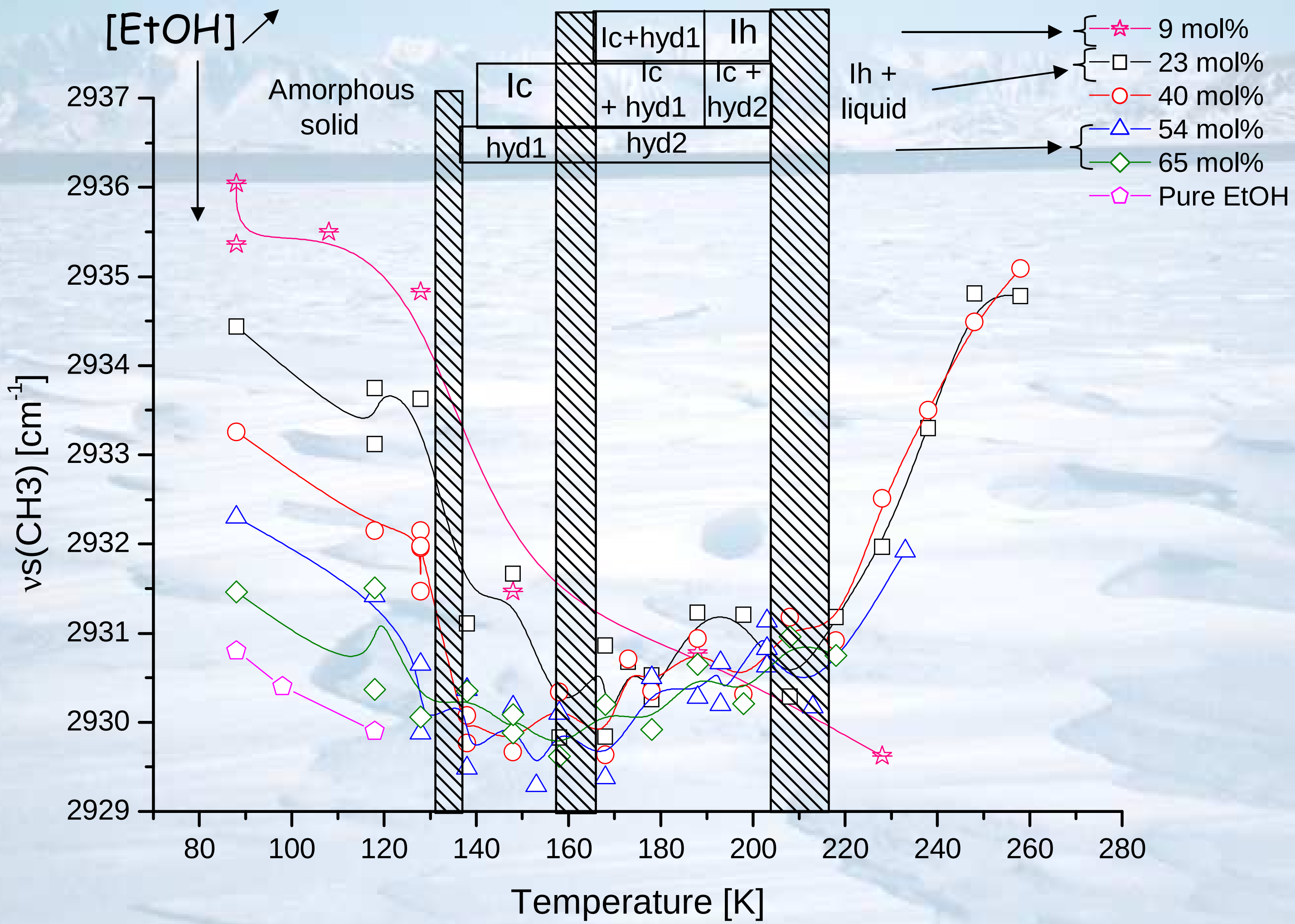
Chazallon et al. Vib. Spectrosc. (2006)

Raman spectra of co-deposited EtOH and EtOH:H_2O



Chazallon et al. PCI proc. (2007)

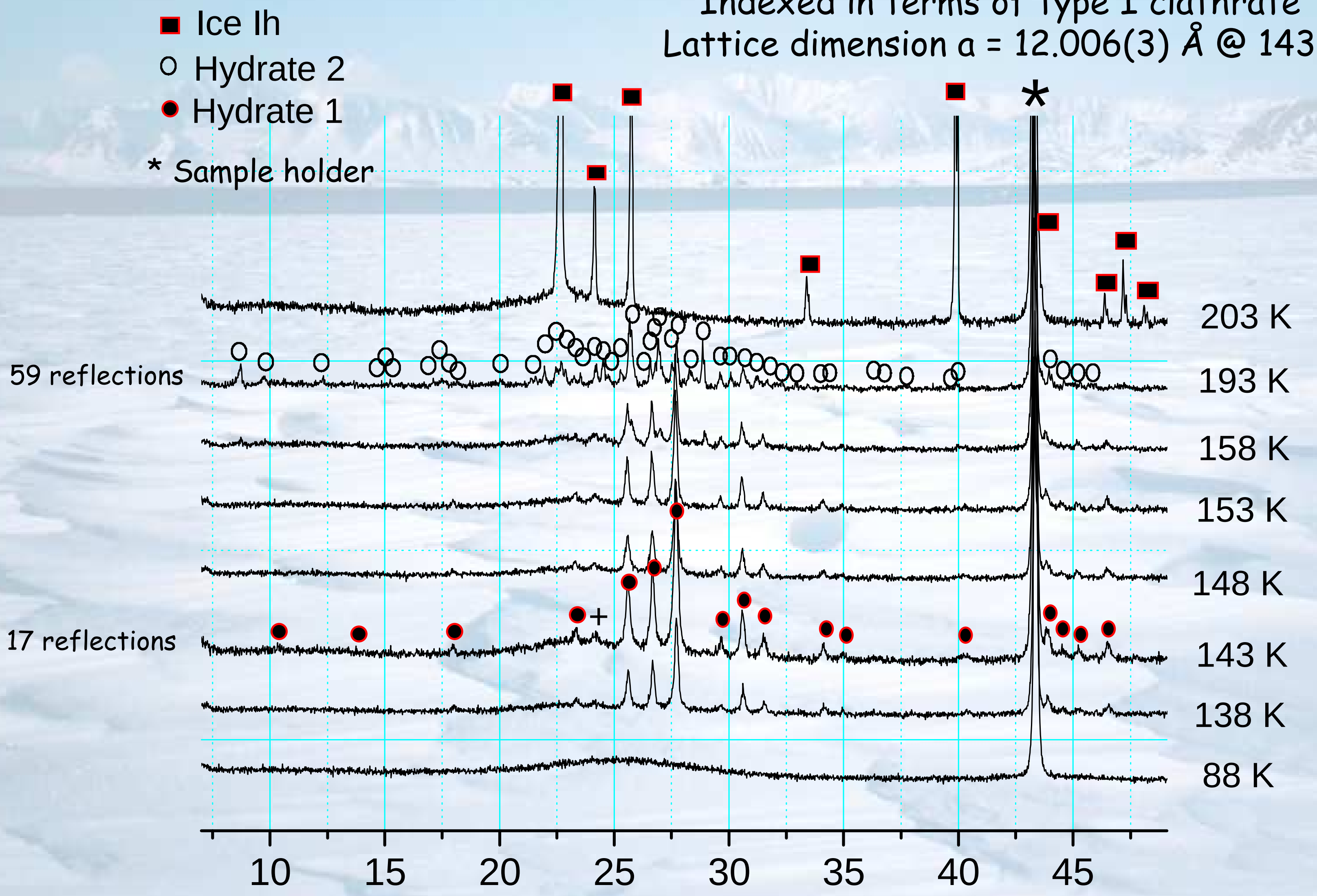
4. $\nu_S(CH_3)$



Chazallon et al. PCI (2007) conf. Proc.

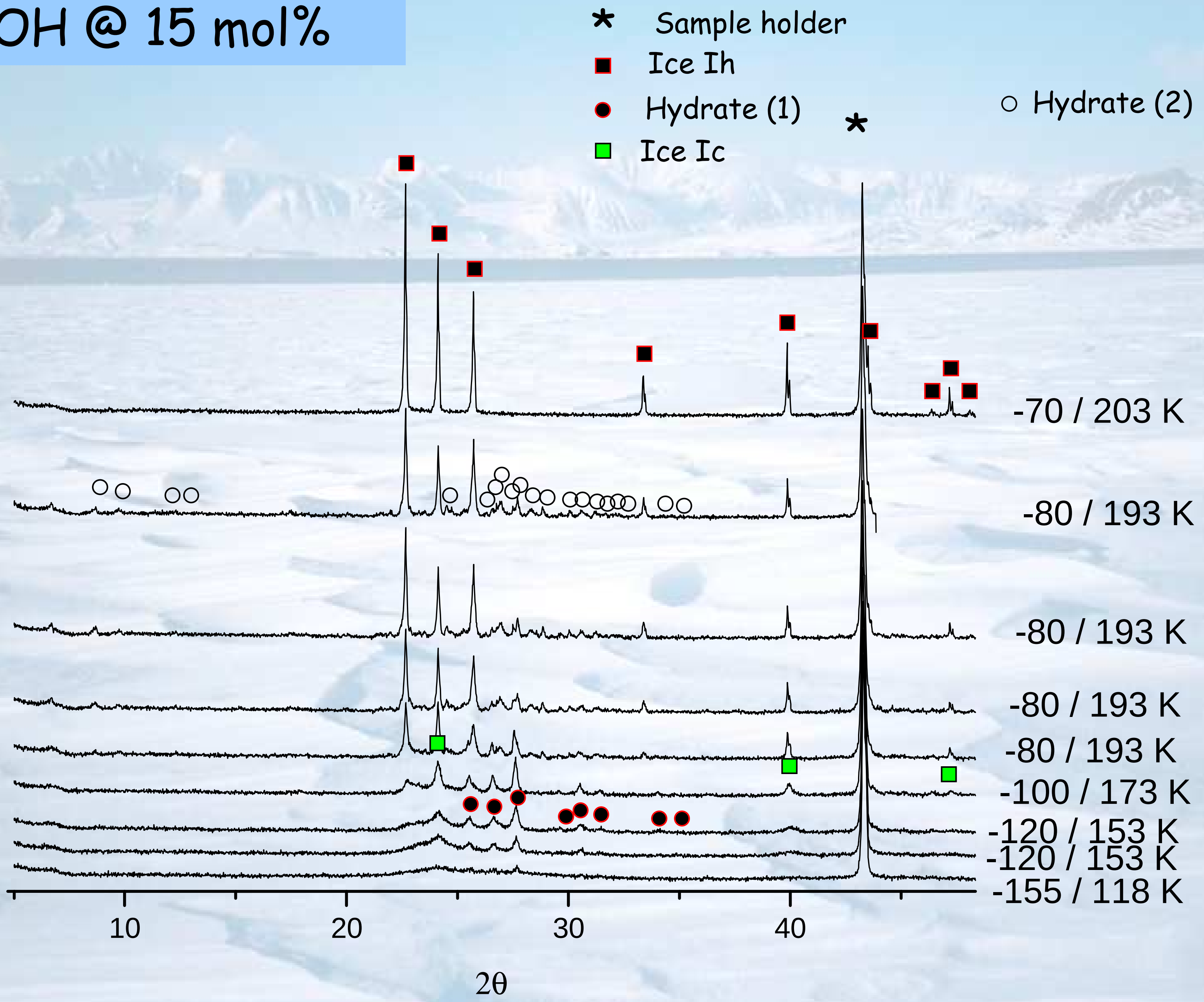
EtOH @ 31 mol%

Hydrate 1 = cubic
Indexed in terms of type I clathrate
Lattice dimension a = 12.006(3) Å @ 143 K

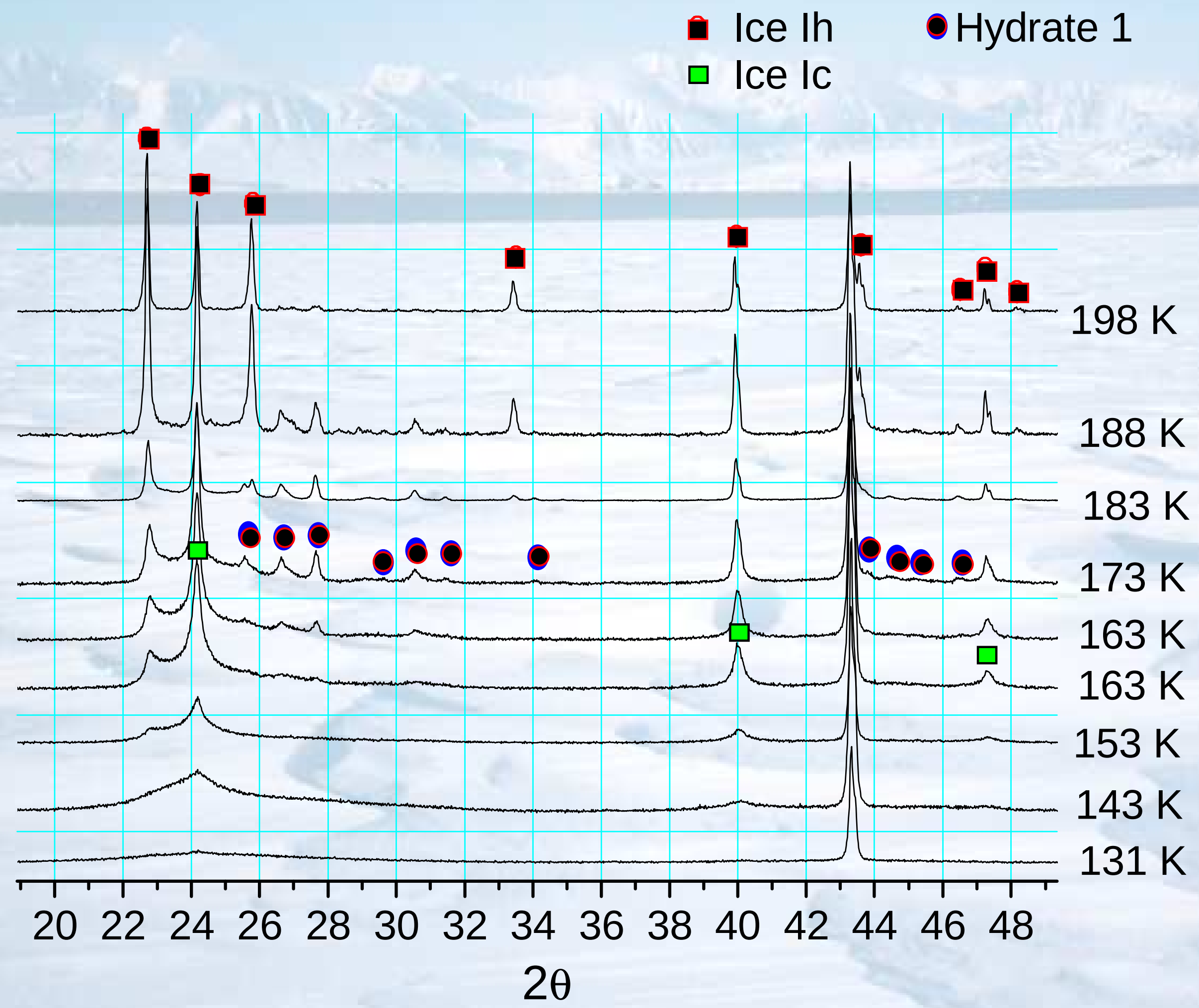


Chazallon et al. PCI (2007) conf. Proc.

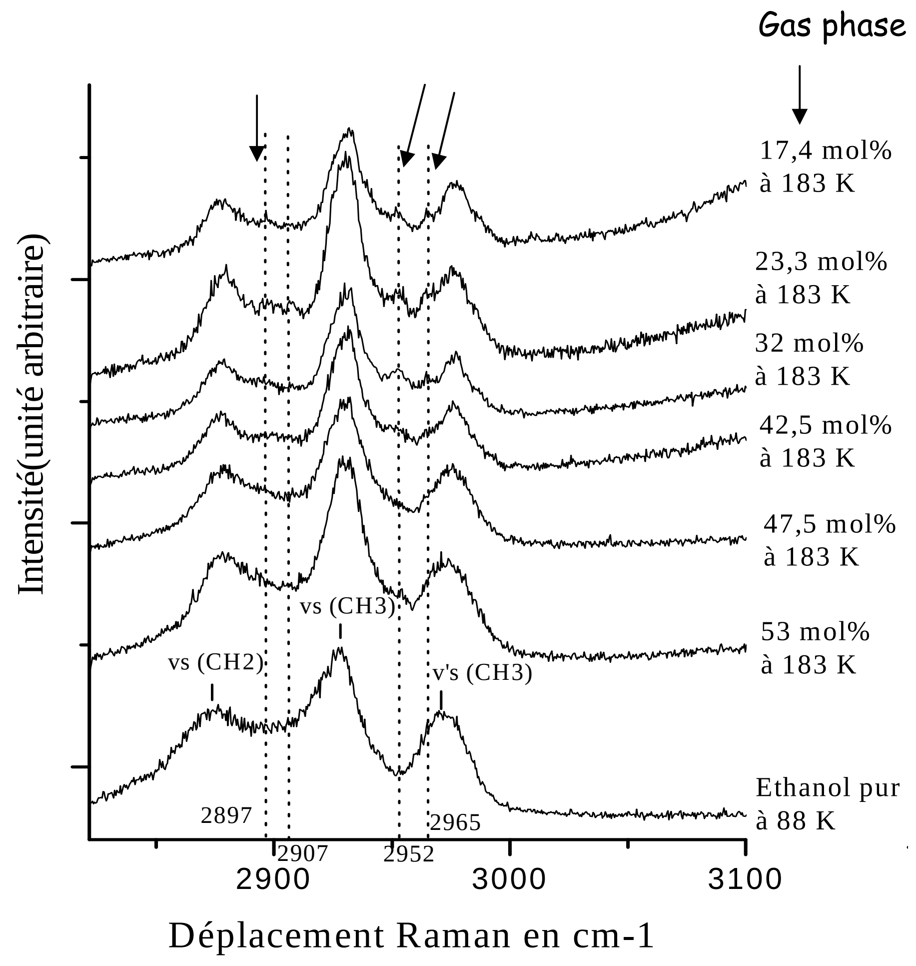
EtOH @ 15 mol%

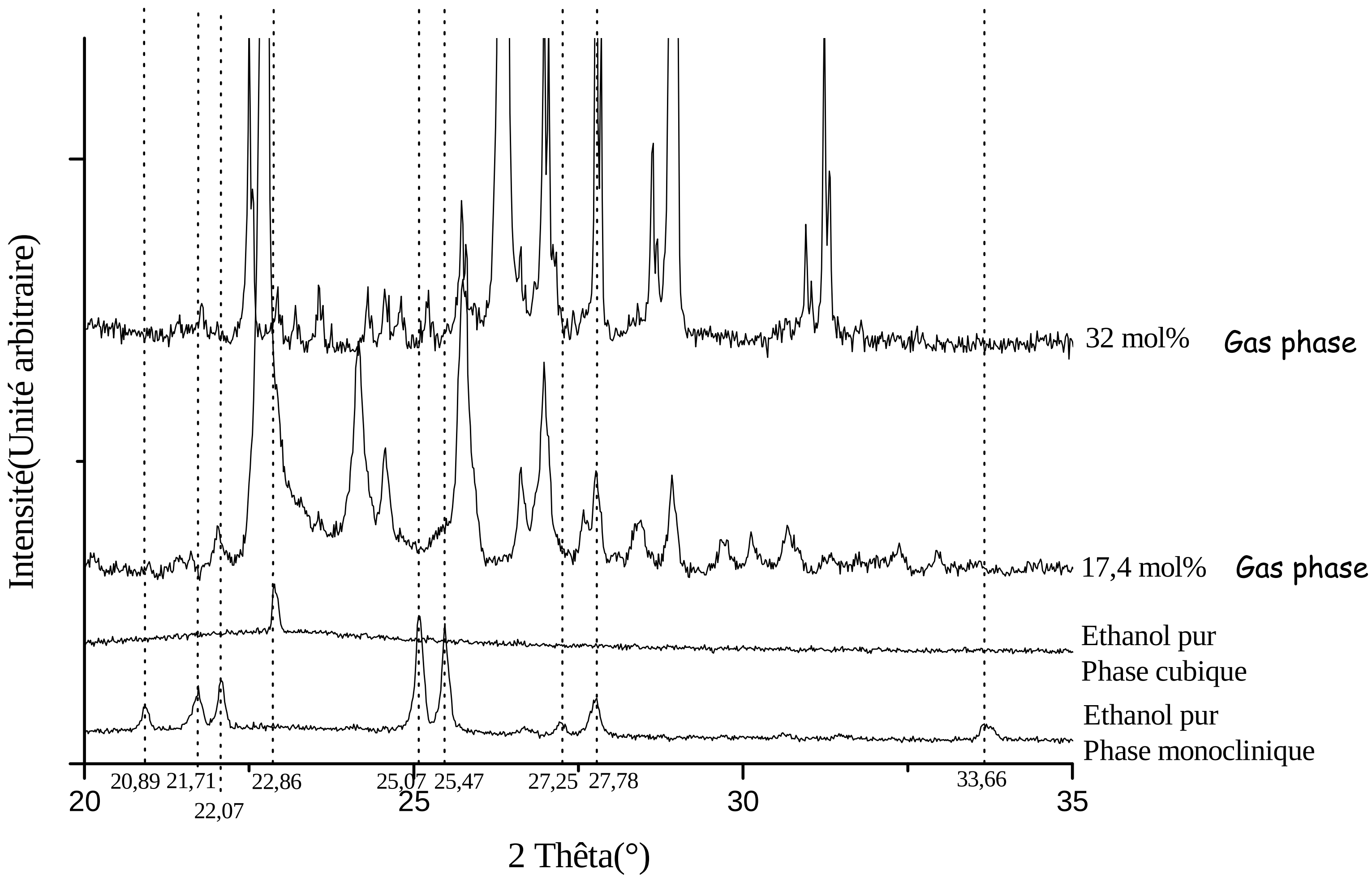

* Sample holder
Ice Ih
Hydrate (1)
Ice Ic
Hydrate (2)
*
-70 / 203 K
-80 / 193 K
-80 / 193 K
-80 / 193 K
-80 / 193 K
-100 / 173 K
-120 / 153 K
-120 / 153 K
-155 / 118 K
10
20
30
40
2θ

EtOH @ 4 mol%

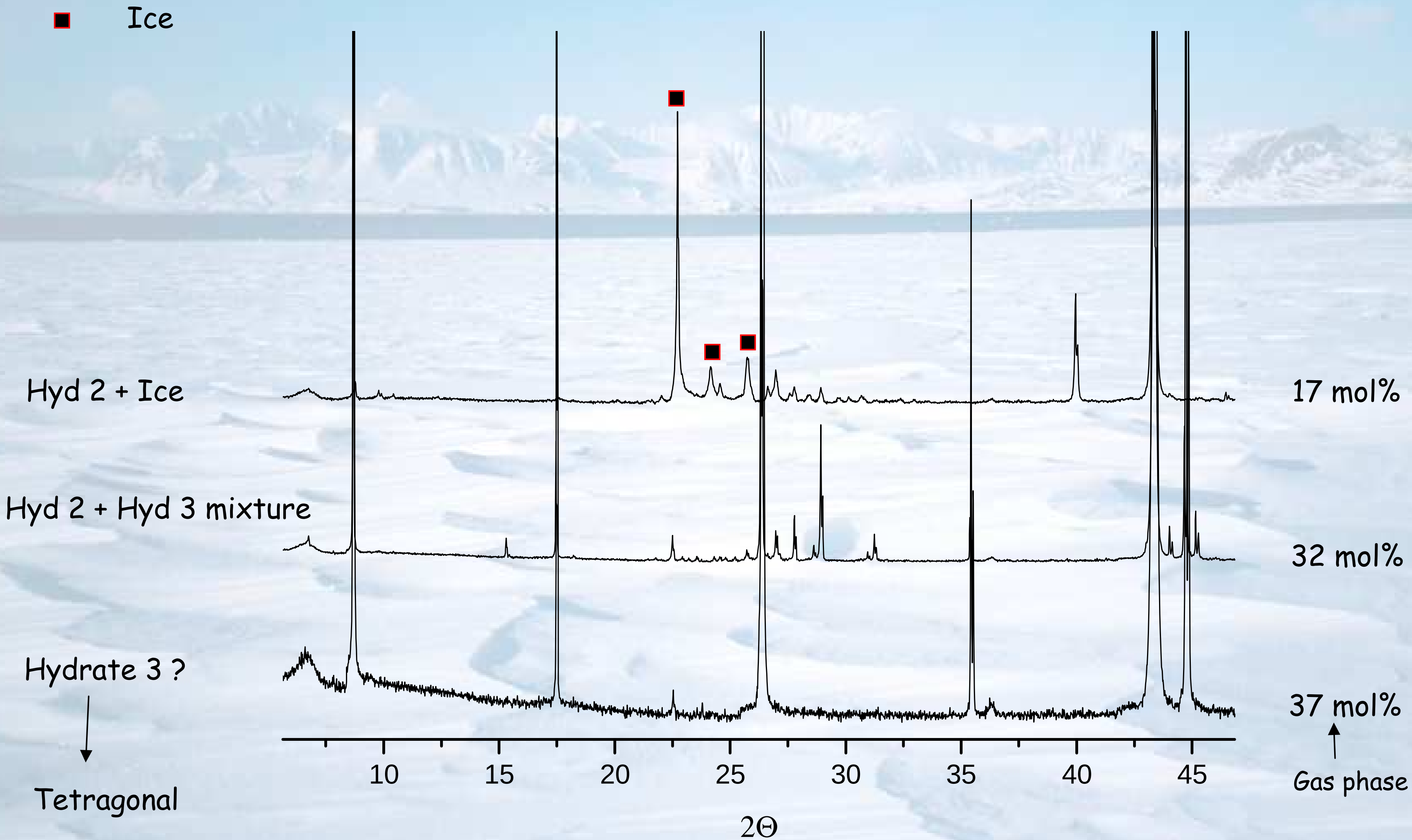

Ice Ih
Hydrate 1
Ice Ic
198 K
188 K
183 K
173 K
163 K
163 K
153 K
143 K
131 K
20 22 24 26 28 30 32 34 36 38 40 42 44 46 48
2θ

Deposition @ 183 K




Intensité(Unité arbitraire)
2 Thêta(°)
20
25
30
35
20,89
21,71
22,07
22,86
25,07
25,47
27,25
27,78
33,66
32 mol%
Gas phase
17,4 mol%
Gas phase
Ethanol pur
Phase cubique
Ethanol pur
Phase monoclinique

Deposition @ 183 K



Summary

Co-deposition:

•Formaldehyde

-Formaldehyde distributed molecularly in ASW @ 88 K, escape at ~ 140 K
-Influence of external gas pressure (1 atm of N_2)
-Highly polar surface (dangling OH bonds?) and micro-porosity facilitate the adsorption and incorporation of N_2 gas in the structure
-No N_2 in the structure when added @ T ~ 120K (no porosity)

-H2CO(s) at ~ 140 K (phase separation)
-Formaldehyde hydrate at ~ 150 K, mixed with incorporated N_2
-Variation in N_2 / H_2CO ratio → different clathrate hydrate structures

•Ethanol:

- Catalytic action of EtOH: T° of crystallization ↘ T< 140 K as [EtOH] ↗)
-2 distinct EtOH-hydrate phases
-Direct crystallization @ 183 K → new hydrate phase

Perspective

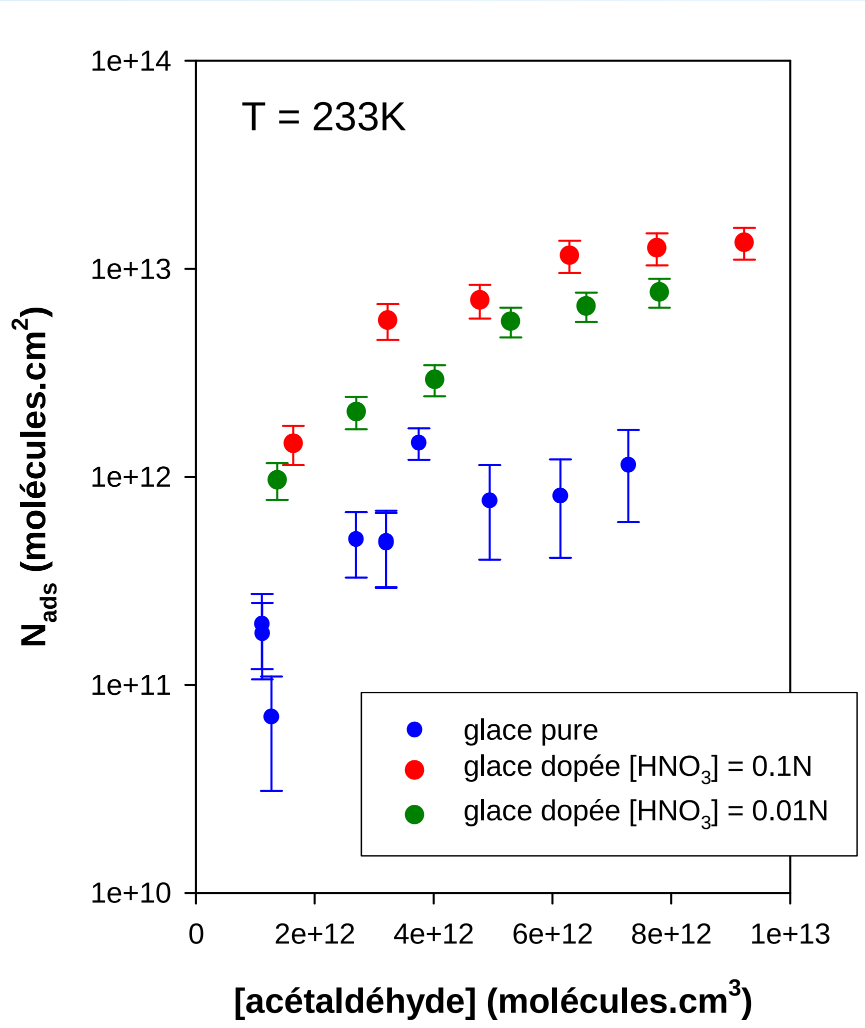
- Solubility of VOC in ice at T° ~ 210-240 K
- Solubility of VOC in acid doped ice

Thanks to

C. Focsa, M. Ziskind, C. Toubin
A. Oancea, S. Facq

Y. Guinet, F. Capet, F. Vitse

B. Hanoune

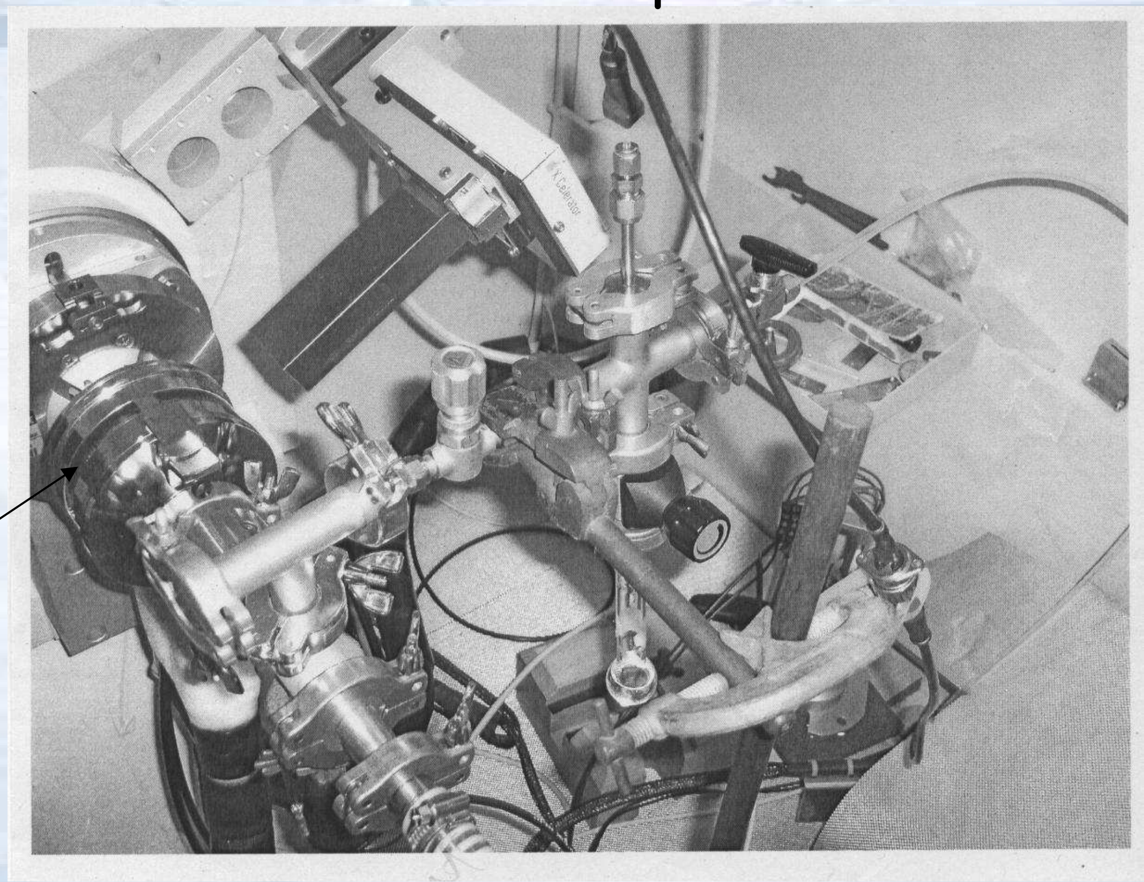


Le Calvé et al.

6. Diffraction X

Powder diffractometer
Xpert-Pro Panalytical
Configuration Θ-Θ
(Collaboration **LDSMM**,
Y.Guinet, F. Capet)

Set-up

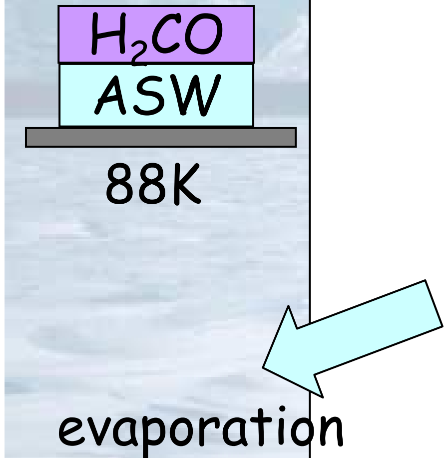


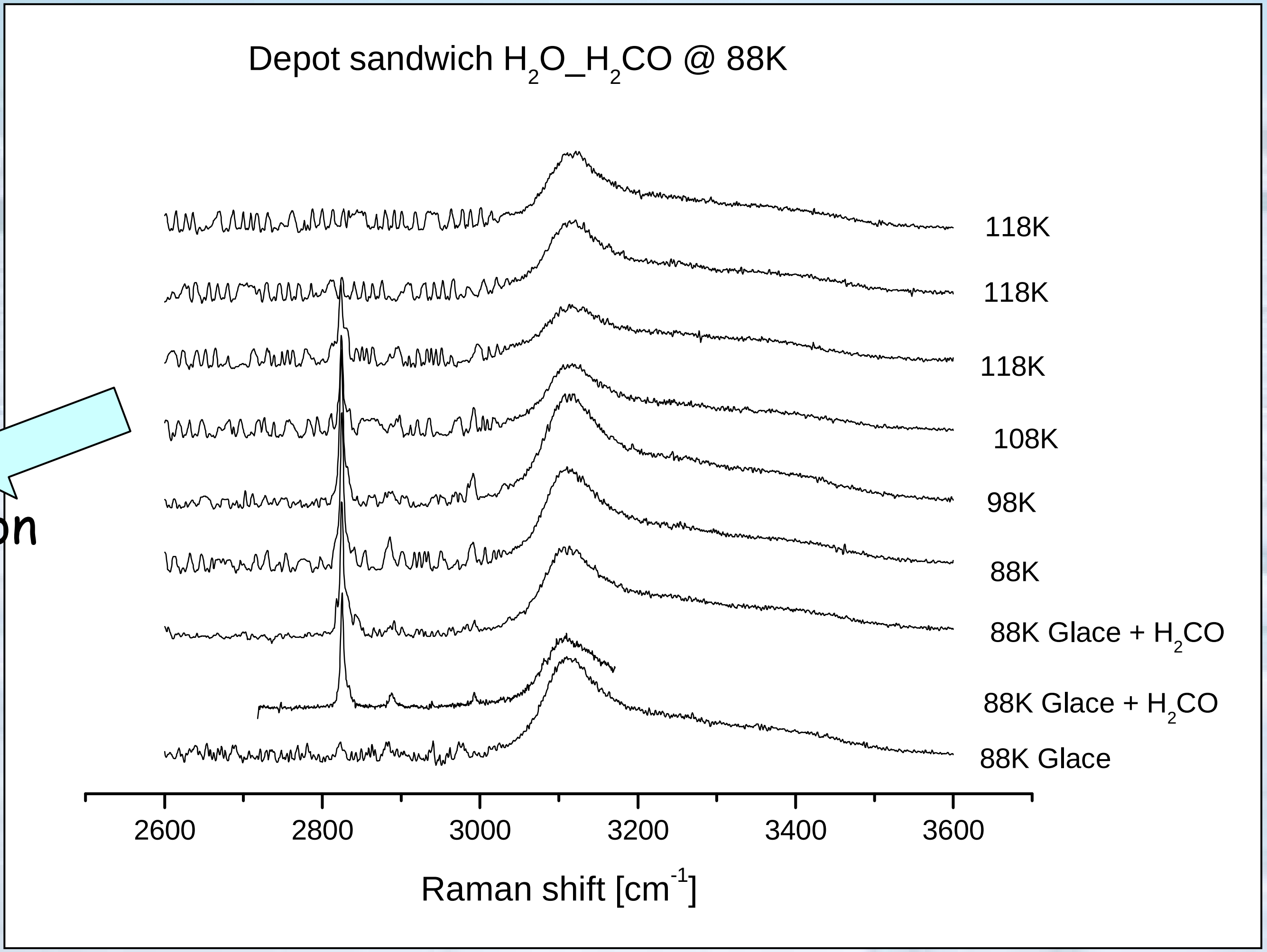
Cryogenic chamber

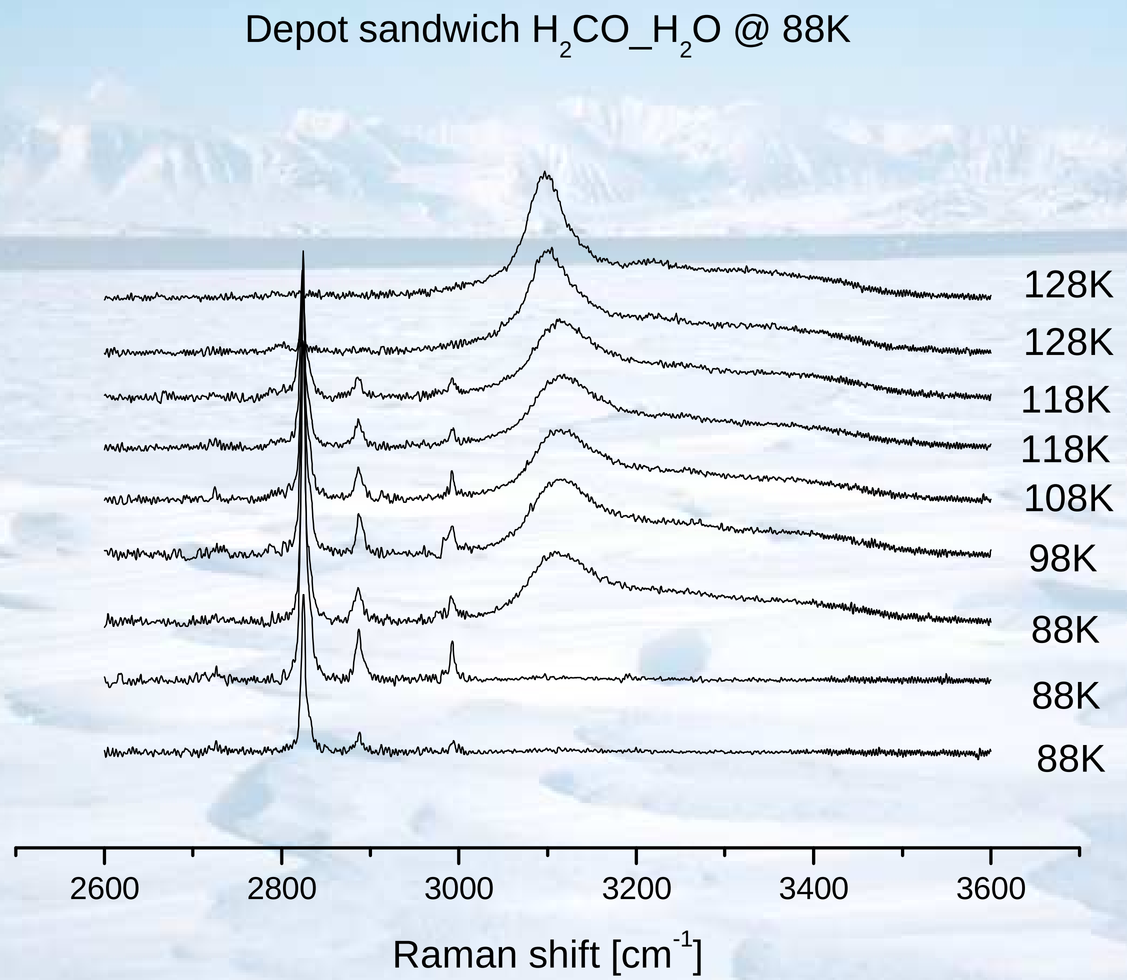
Regulation +/- 0.5 K

rate: 0.5 K to 10 K /min

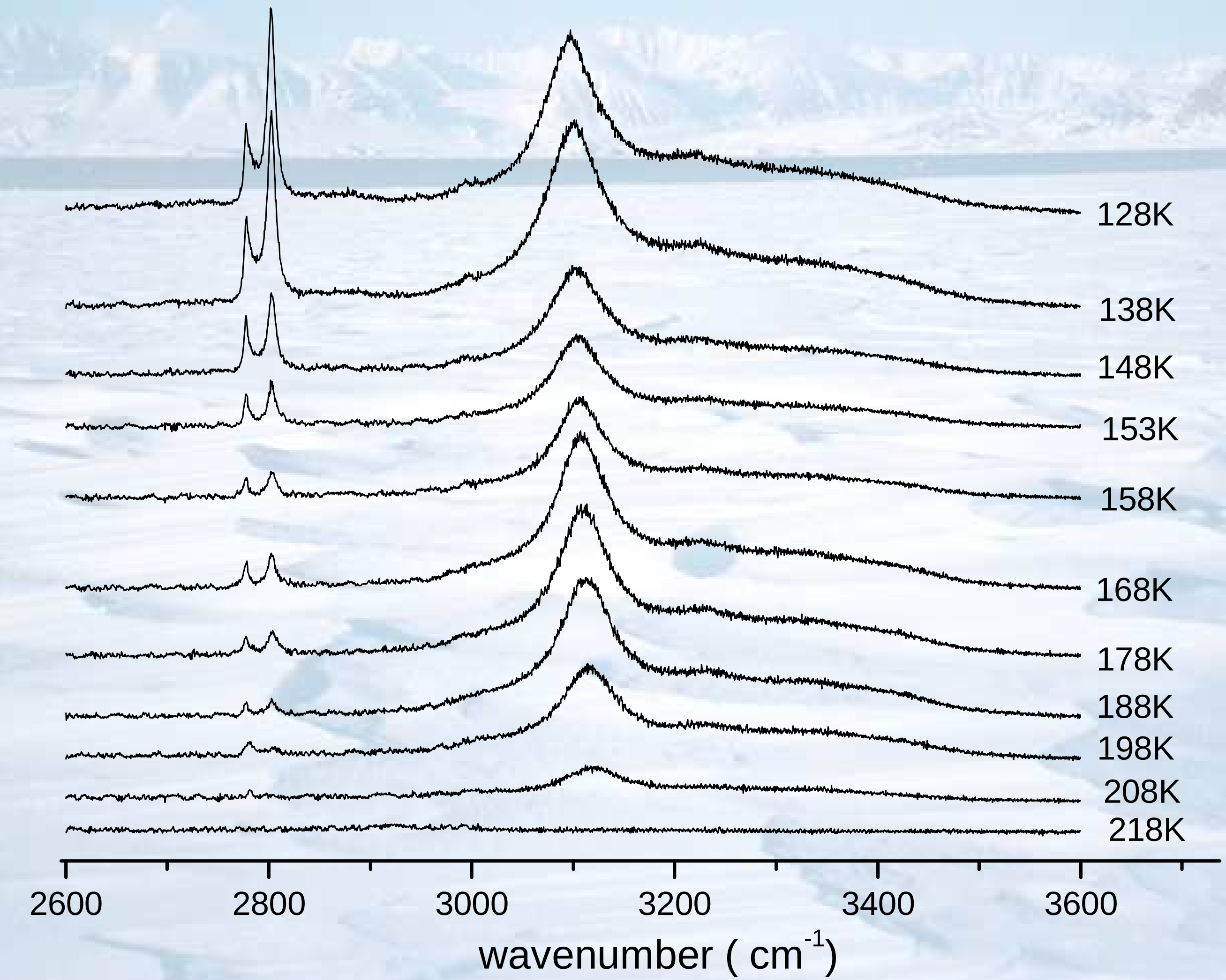
Variable T° 273-77 K


H2CO
ASW
88K
evaporation


Depot sandwich H2O_H2CO @ 88K
118K
118K
118K
108K
98K
88K
88K Glace + H2CO
88K Glace + H2CO
88K Glace
2600
2800
3000
3200
3400
3600
Raman shift [cm-1]

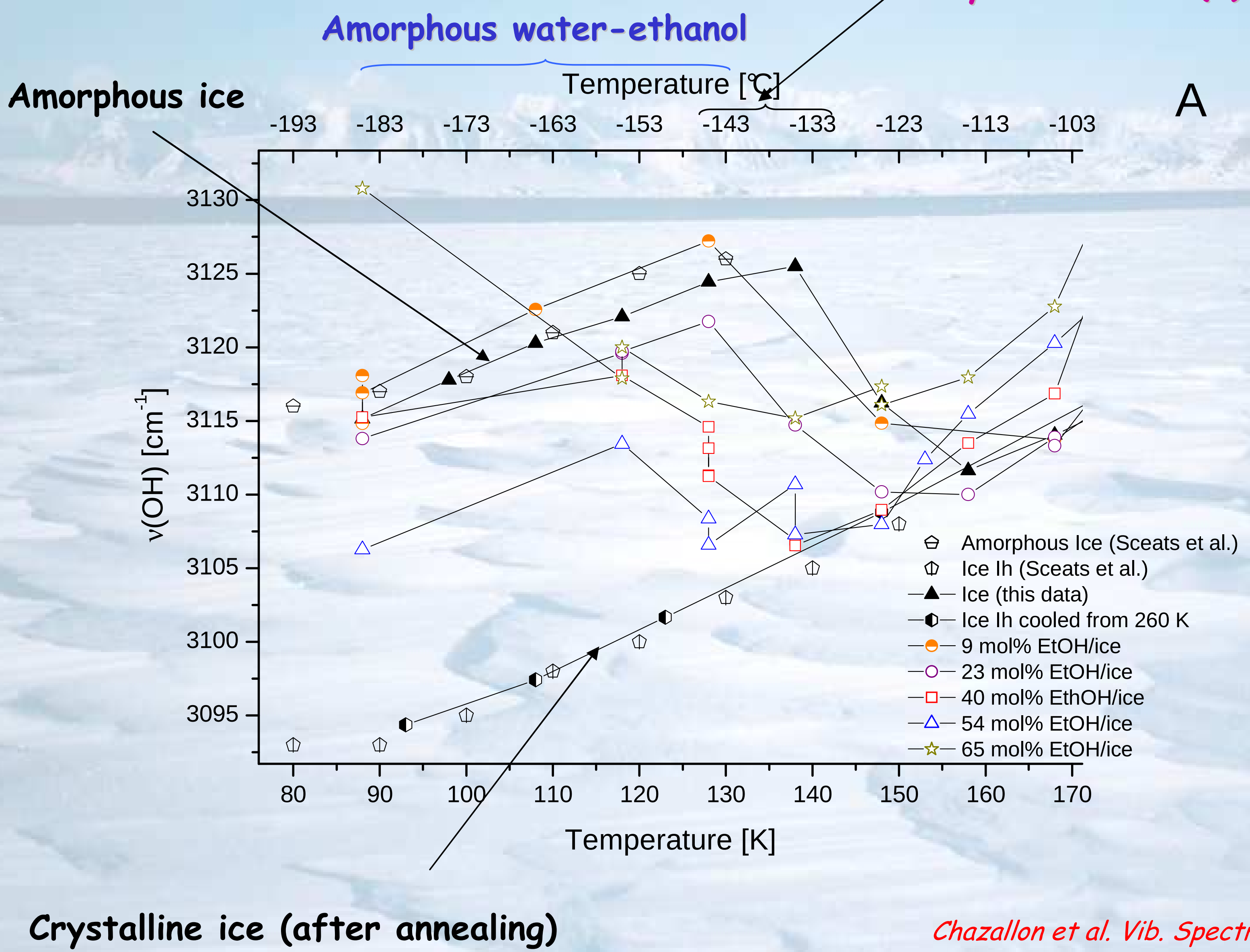

Depot sandwich H2CO_H2O @ 88K
128K
128K
118K
118K
108K
98K
88K
88K
88K
2600
2800
3000
3200
3400
3600
Raman shift [cm-1]

Co-deposition H_2O:H_2CO 6:1 @ 128 K

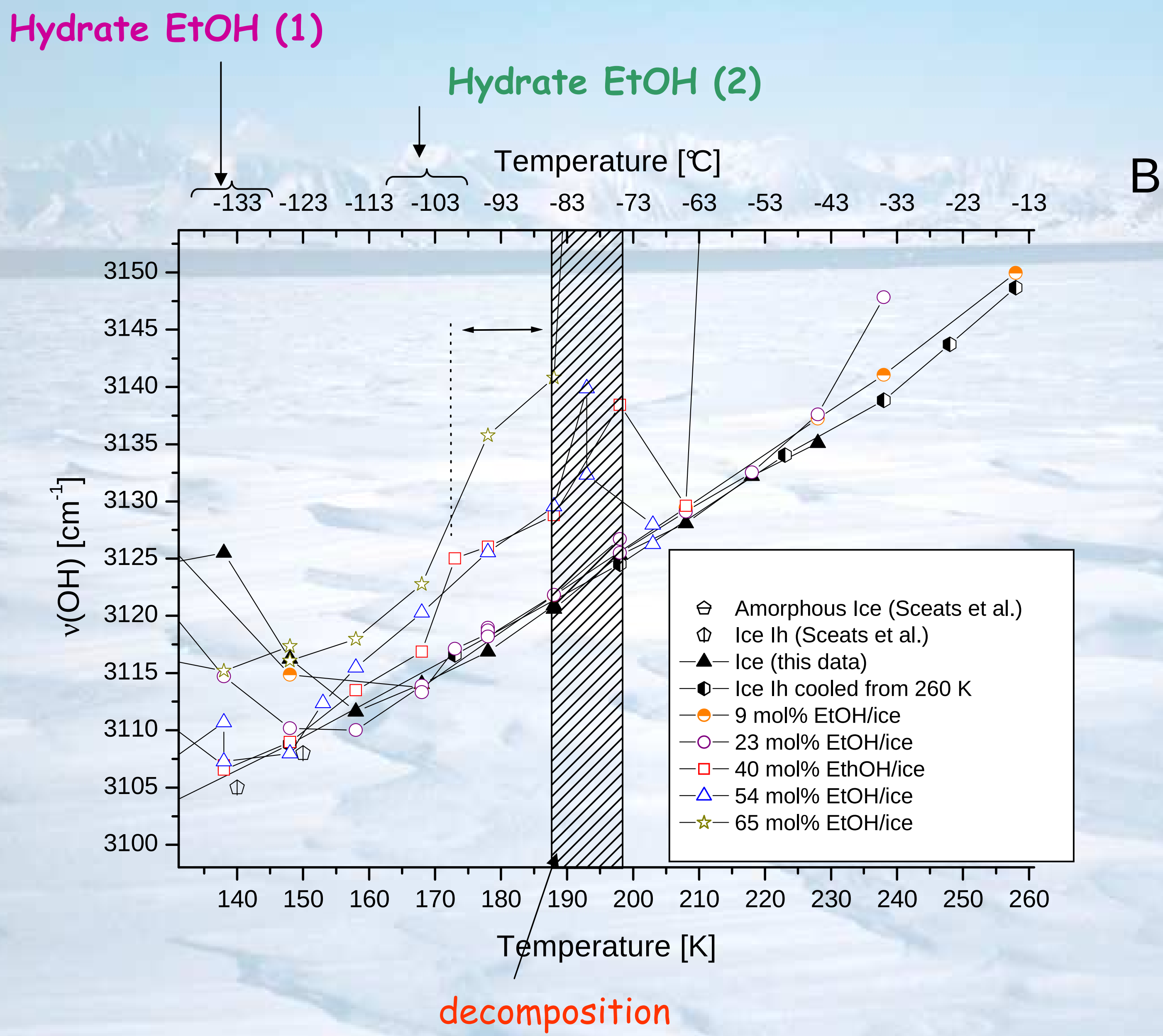


Co-dépôt
H_2CO/H2O

3. ν(OH): Evolution with T°



Chazallon et al. Vib. Spectrosc. (2006)

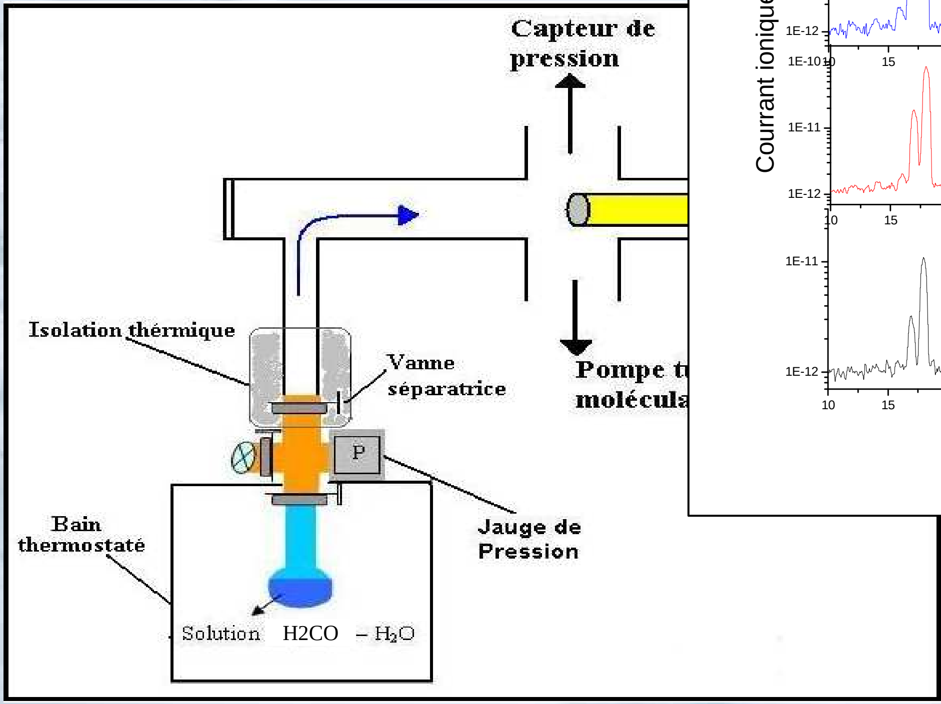

Hydrate EtOH (1)
Hydrate EtOH (2)
Temperature [℃]
B
-133
-123
-113
-103
-93
-83
-73
-63
-53
-43
-33
-23
-13
ν(OH) [cm-1]
3150
3145
3140
3135
3130
3125
3120
3115
3110
3105
3100
140
150
160
170
180
190
200
210
220
230
240
250
260
Temperature [K]
Amorphous Ice (Sceats et al.)
Ice Ih (Sceats et al.)
Ice (this data)
Ice Ih cooled from 260 K
9 mol% EtOH/ice
23 mol% EtOH/ice
40 mol% EthOH/ice
54 mol% EtOH/ice
65 mol% EtOH/ice
decomposition

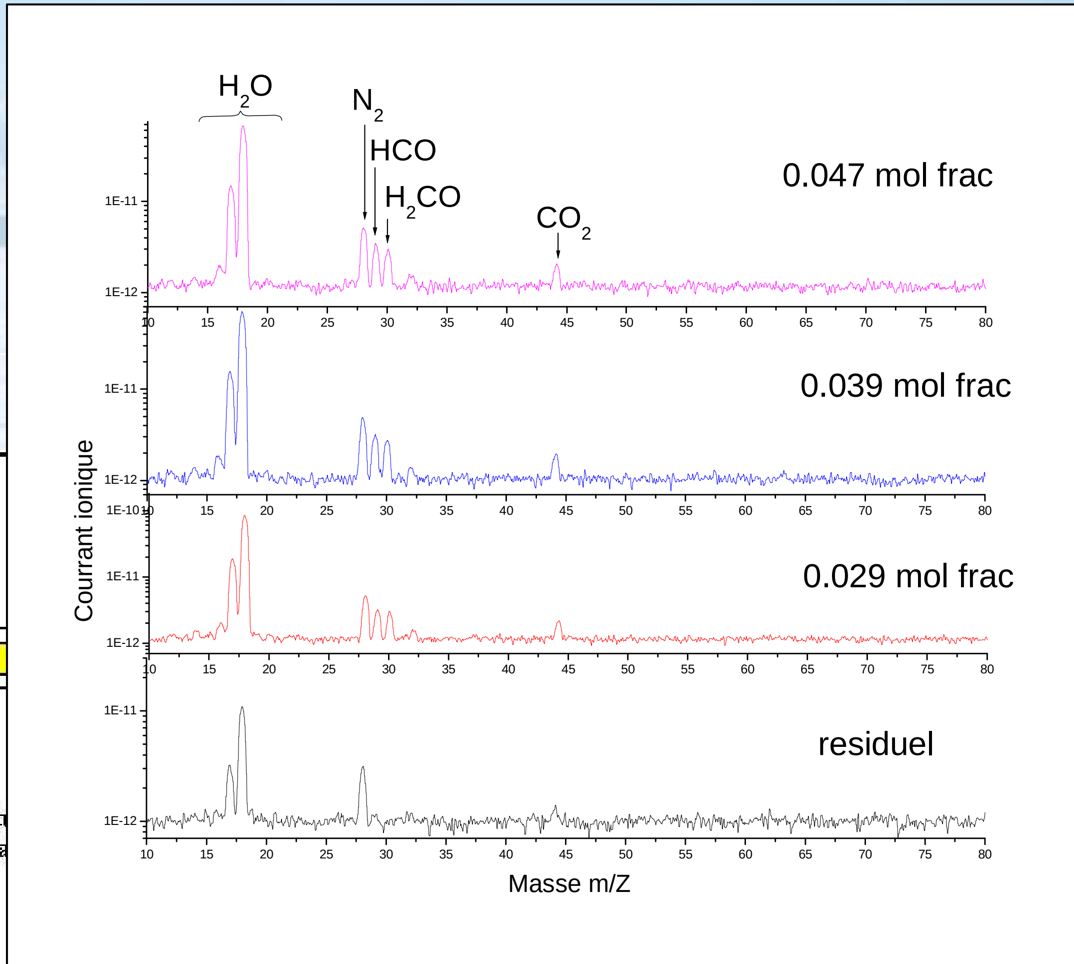
1. Gas + condensed phase composition of H_2O:H_2CO

Mass spectrometry:

Gas Phase: H_2O+ H_2CO

Liquide Phase:
oligomers ($HO(H_2CO)_nH$)

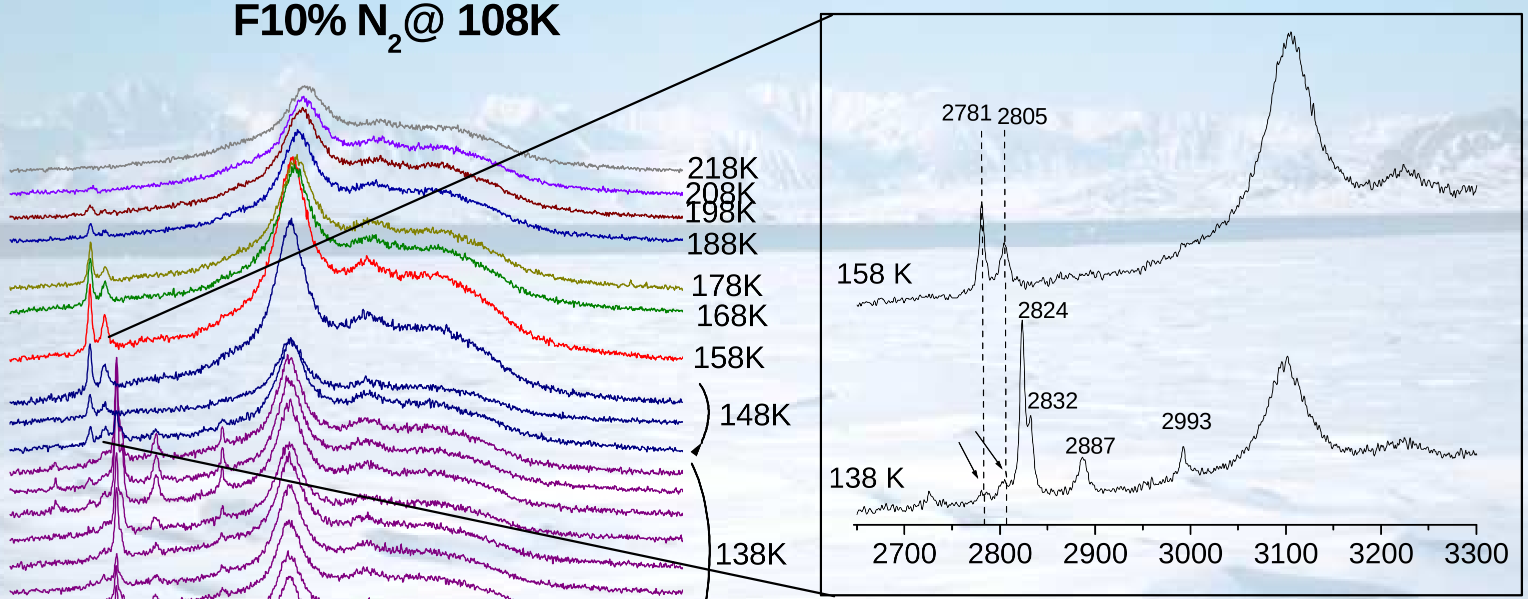


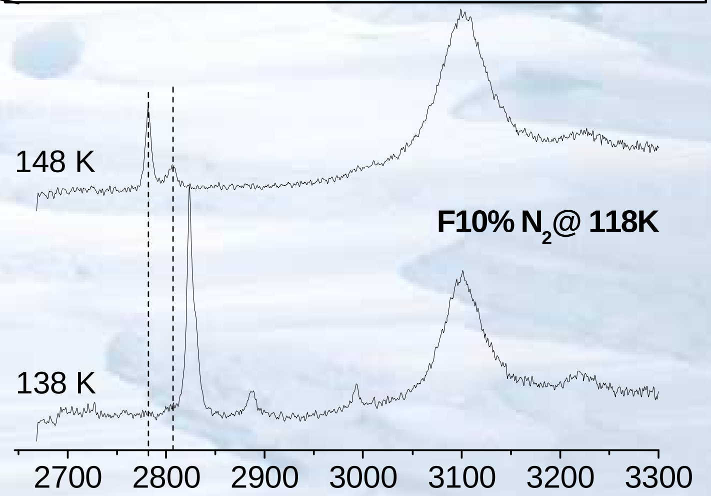


M_{48} ($HOCH_2OH$) absent

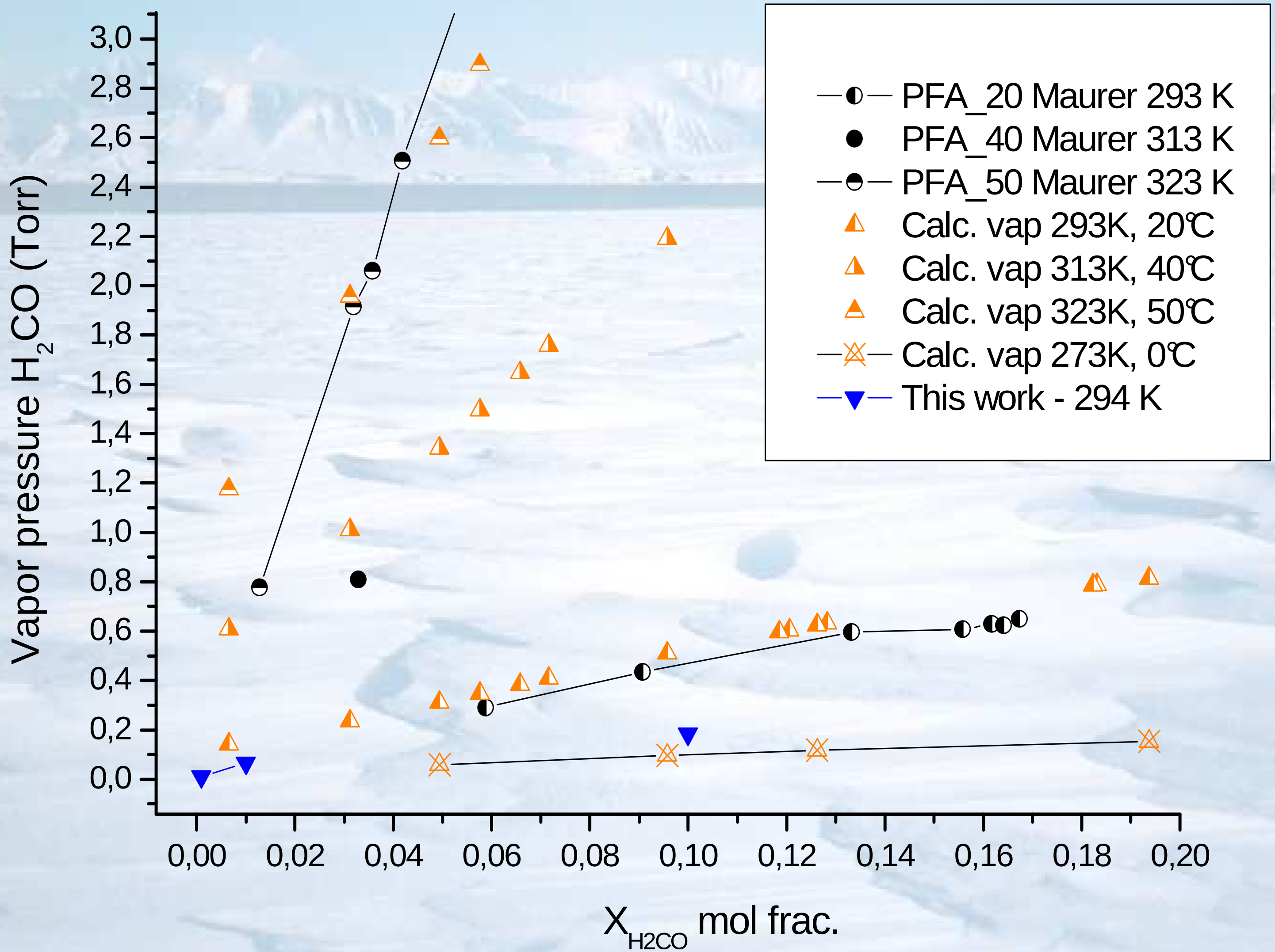
next talk!

Influence of external gas phase conditions



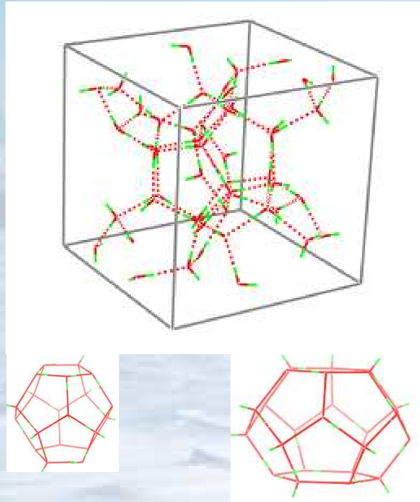


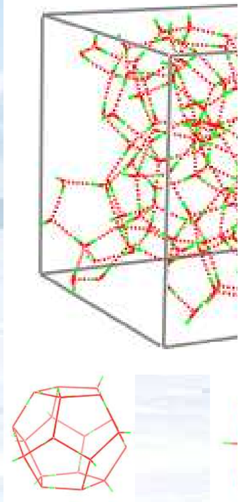
HCHO-hydrates free of Nitrogen


Vapor pressure H2CO (Torr)
3,0
2,8
2,6
2,4
2,2
2,0
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0,00
0,02
0,04
0,06
0,08
0,10
0,12
0,14
0,16
0,18
0,20
XH2CO mol frac.
PFA_20 Maurer 293 K
PFA_40 Maurer 313 K
PFA_50 Maurer 323 K
Calc. vap 293K, 20℃
Calc. vap 313K, 40℃
Calc. vap 323K, 50℃
Calc. vap 273K, 0℃
This work - 294 K

Ol

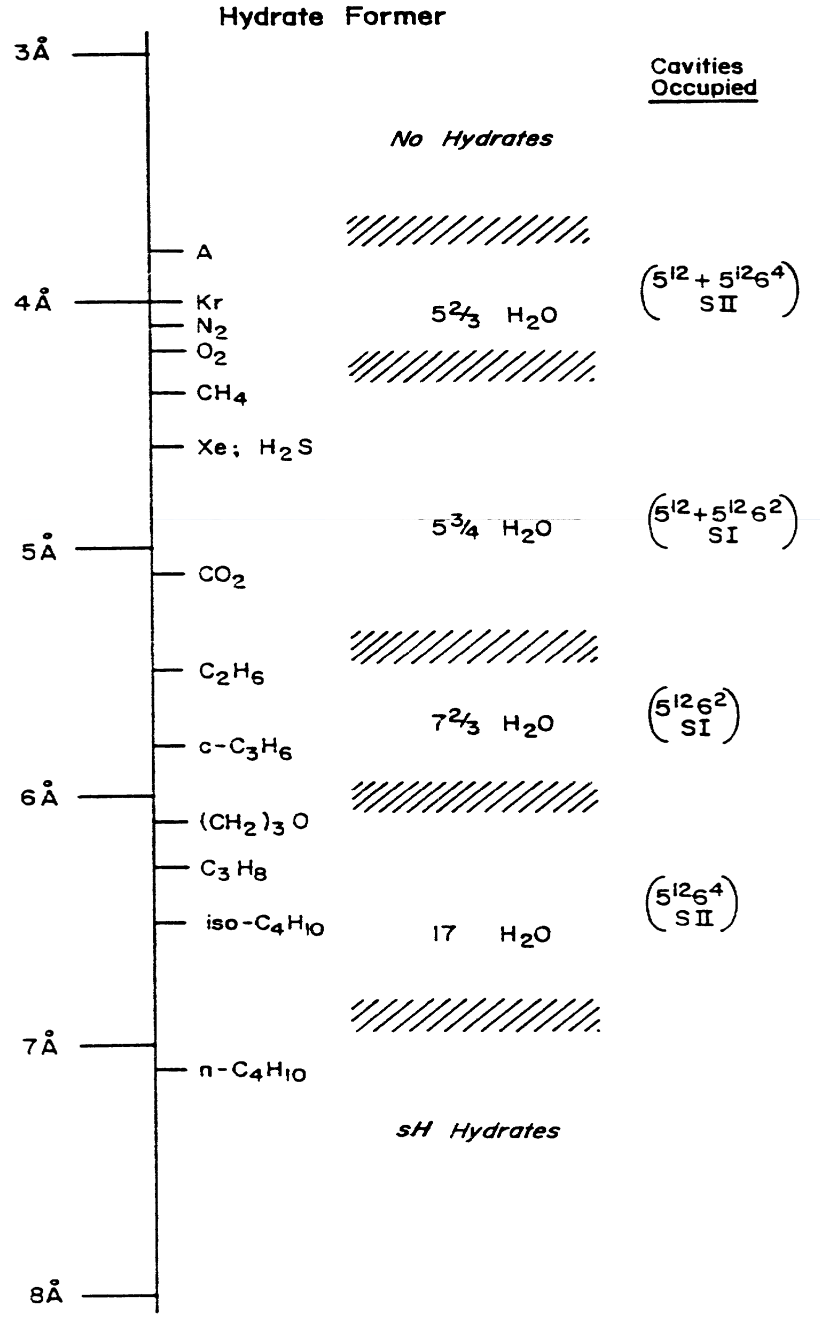
Classification with the size of gas molecule





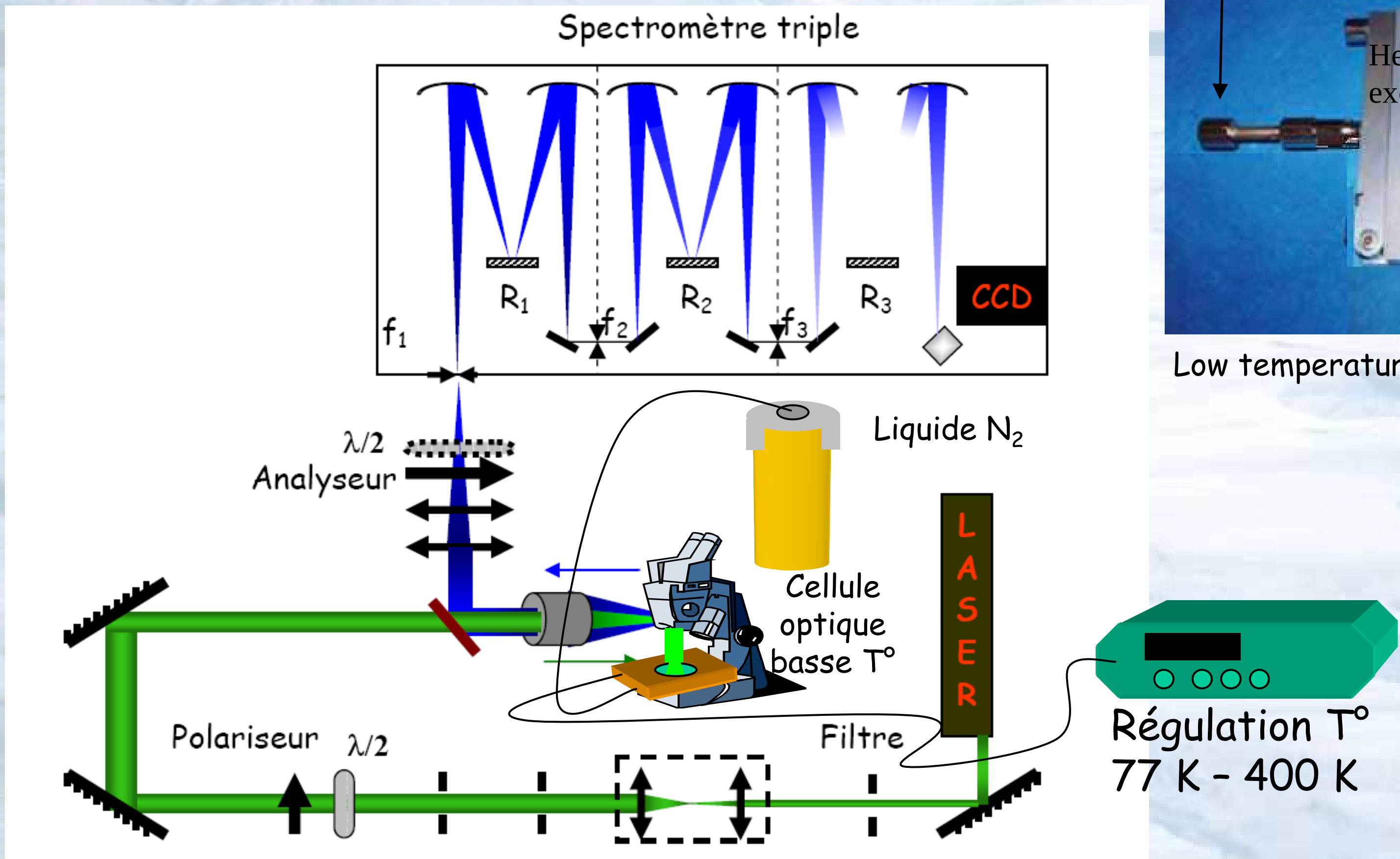
2 + 6 **16 +**

I		Structure	II
Small	Large	Cavity	Small
5^{12}	$5^{12}6^{2}$	Description	5^{12}
2	6	Numbers of cavities / unit cell	16
3.95	4.33	Mean radius of a cavity (Å)	3.91
20	24	Coordination number	20
46		Number of water molecules / unit cell	136
$G{\cdot}5.75H_2O$		Stœchiometry (max.)	G·5.66l

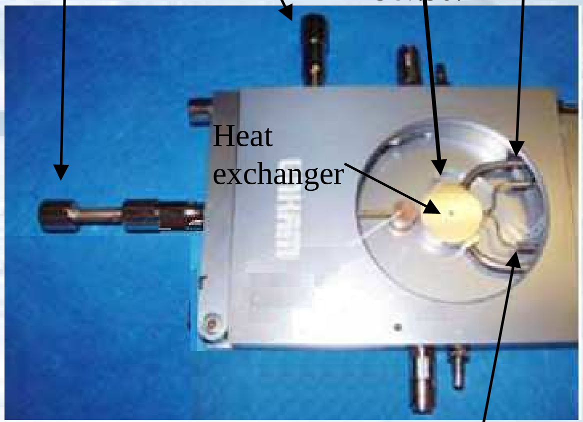


Experimental set-up

Micro-Raman spectroscopy

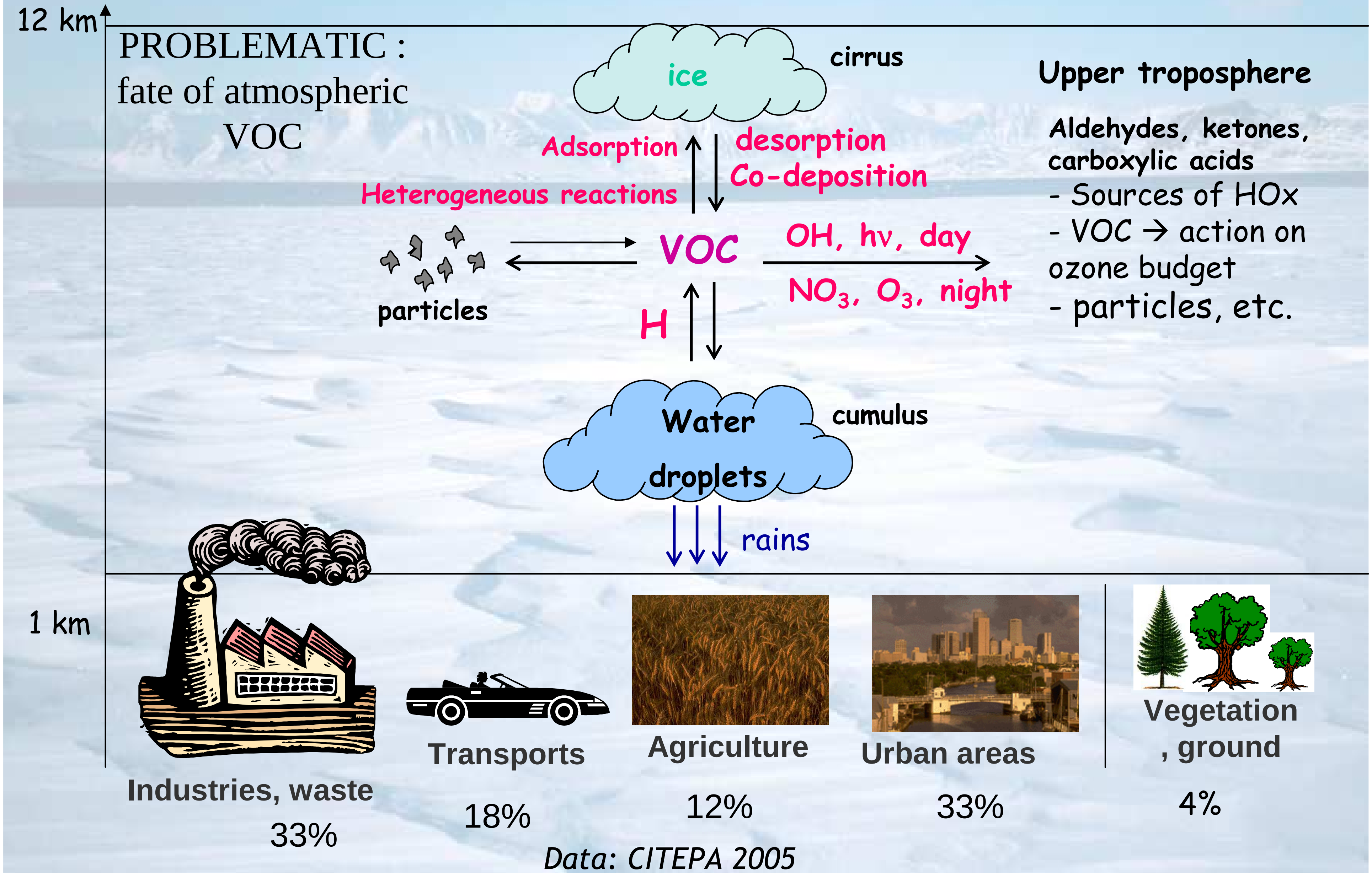


Raman spectrometer



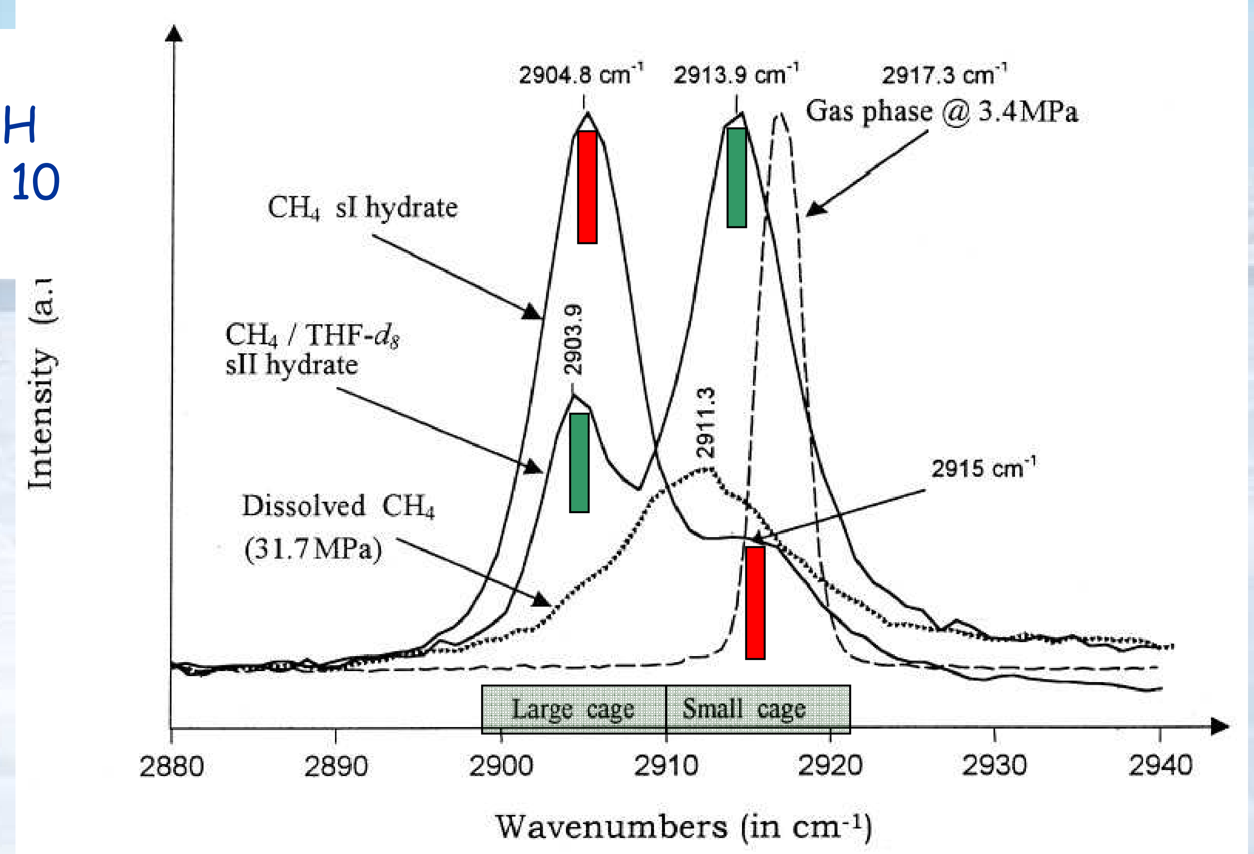
Low temperature stage

Central role of VOC in atmospheric chemistry



Discrimination between different structures

Raman shift and splitting of the C-H band of methane (~ 10 cm^{-1})



Subramanian & Sloan, Fluid Phase Equil. 158-160, 813 (1999)

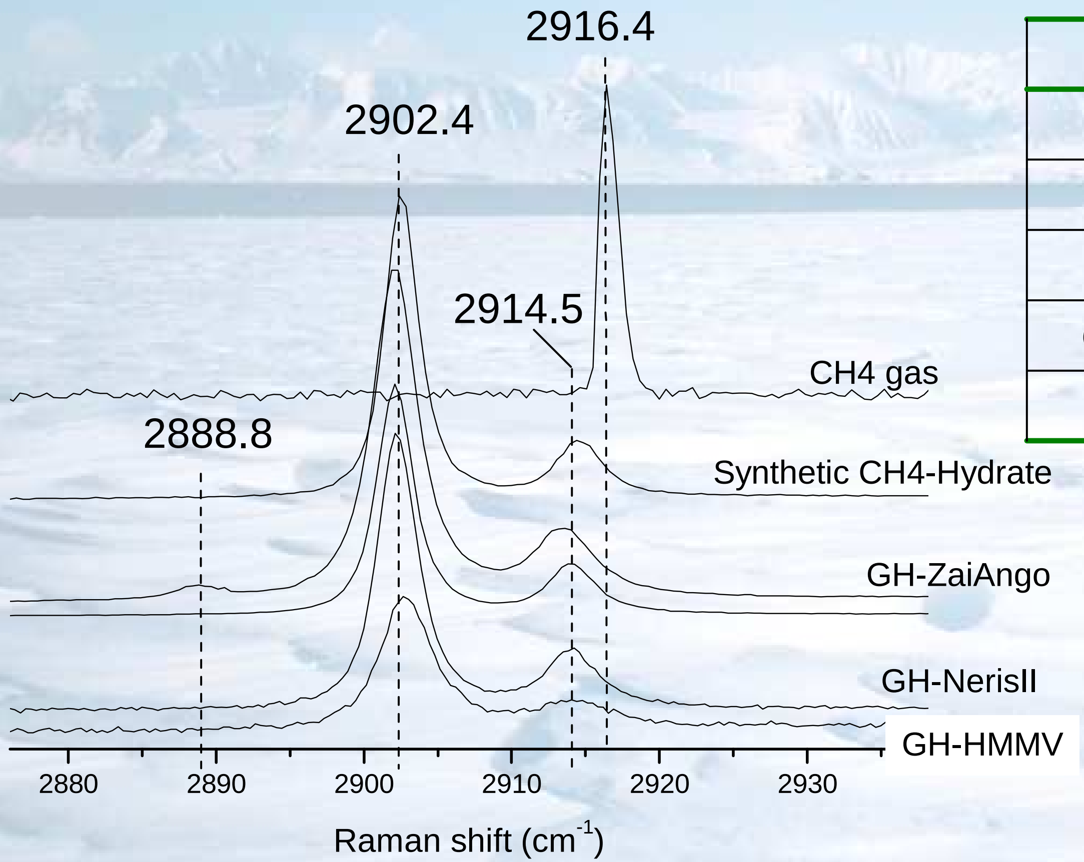
Raman intensity:

$I \propto I_0 N_i \sigma_r f$ →

$\theta_{LC} / \theta_{SC} = I_{LC} / (3\, I_{SC})$ Type I

$\theta_{LC} / \theta_{SC} = (2\, I_{LC}) / I_{SC}$ Type II

Raman spectra of the natural gas hydrates (Congo-Angola margin)



Hydrate	θ_{SC} / θ_{LC}
ZaiAngo	0.86 ± 0.03
Neris II	0.81 ± 0.02
HMMV	0.8 ± 0.1
CH_4-hydrate	0.78 ± 0.02
H_2S-hydrate	0.95 ± 0.1

- Splitting of the C-H stretching
- Downshift / vapor phase

→ Type I

Chazallon et al., Chem. Geol. 2007 (submitted)

Conclusion: importance of in-situ experimental conditions control of (p, T, X)

- Gas incorporation at low pressure:
  - Co-deposition:
    - Amorphous phase @ 88 K → hydrate formation as T increases
    - Catalytic action of EtOH: T_{cryst} ↘ (T< 140 K) as [EtOH] ↗
    - Direct crystallization for deposition @ 180 K (≠ growth mechanism)
    - Influence of external gas pressure
    - Molecular H_2CO isolated by co-deposition (distinct hydrate phases)
    - Micro-porosity facilitate the adsorption and incorporation of N_2 gas in the structure
    - Incorporation of N_2 reduced when added @ T ~ 120K

- Gas incorporation at high pressure:
  - natural samples: methane hydrates structure I
  - Influence of the gas composition on the physical properties

Perspective

- Extension to other p, T, *X* conditions (closer to **atmospheric** conditions)
- Work out conditions for enhanced Raman scattering analysis (detection limit)
- Development of high pressure apparatus to study kinetics of hydrate formation and trapping of CO_2

Thanks to

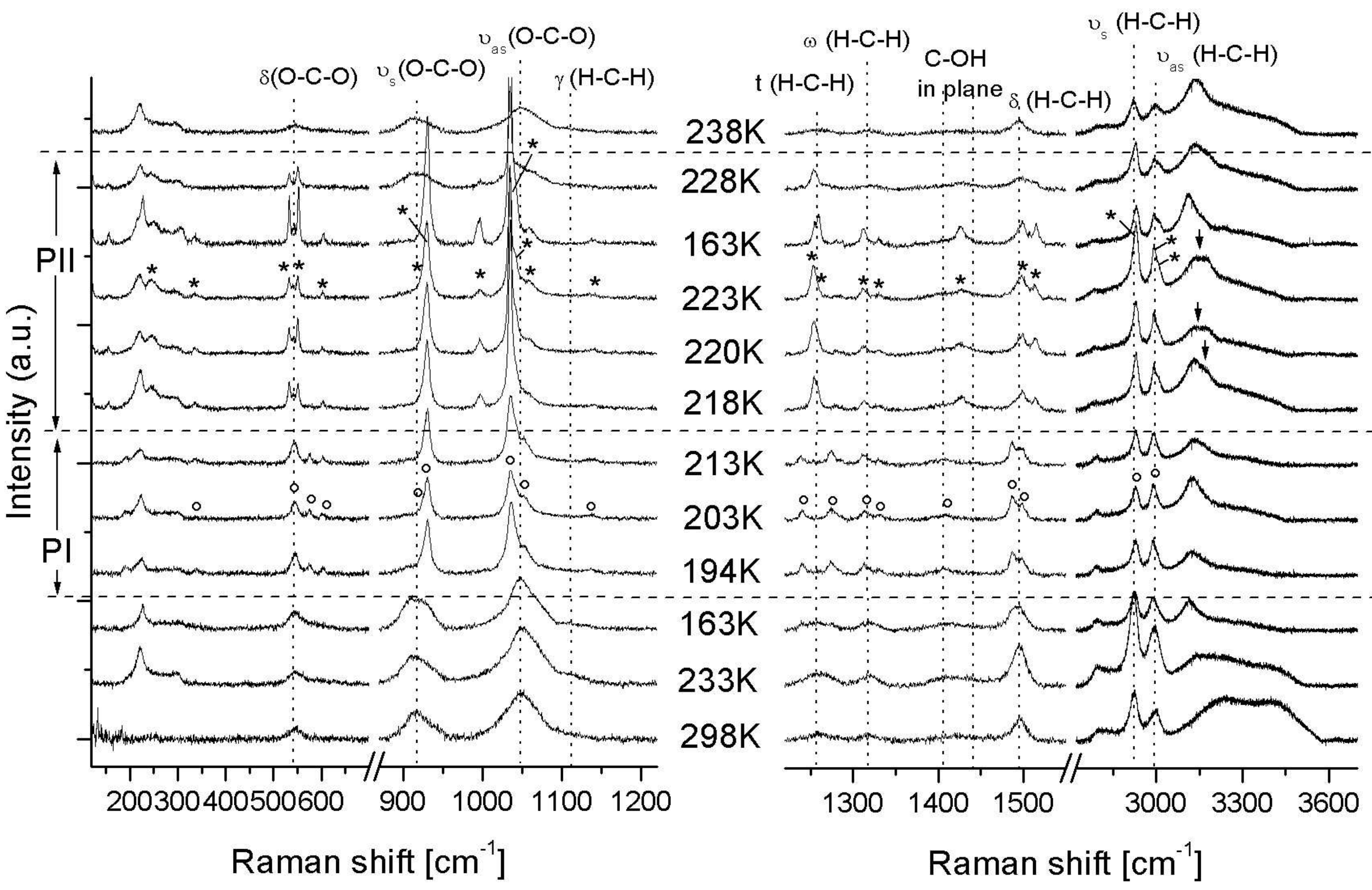
C. Focsa, M. Ziskind, C. Toubin,
A. Oancea, C. Mihesan, S. Facq, Y. Celik

Y. Guinet, F. Capet

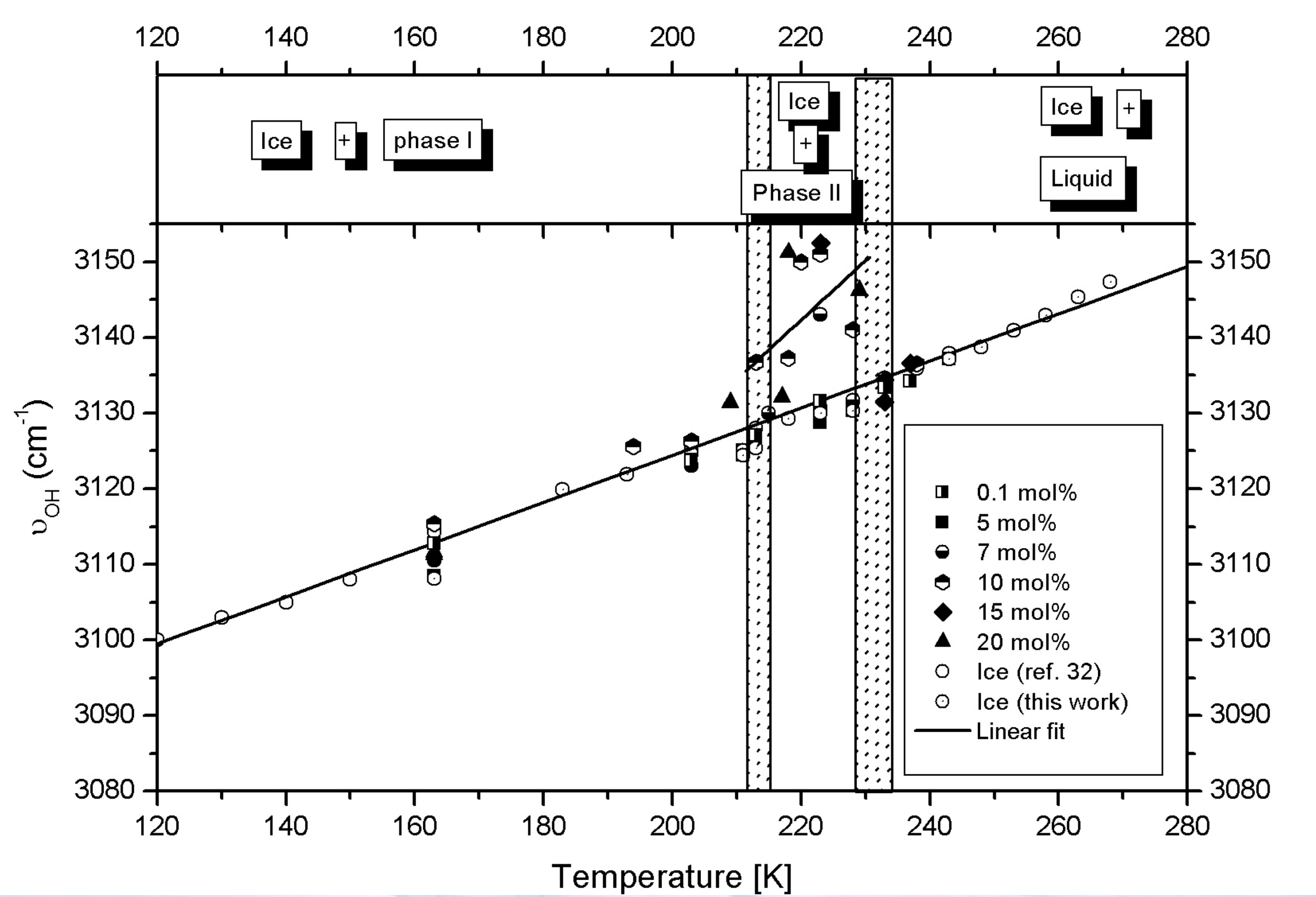
IFREMER Brest – TOTAL FINA ELF

J-L. Charlou, C. Bourry

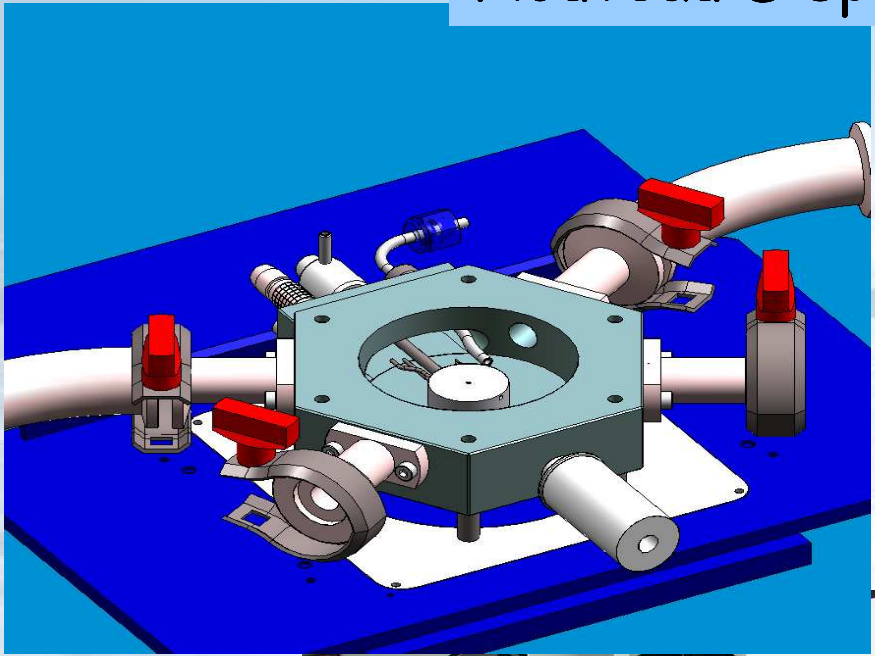
Frozen aqueous solutions H_2CO 10 mol%



Evolution of v(OH) with T°

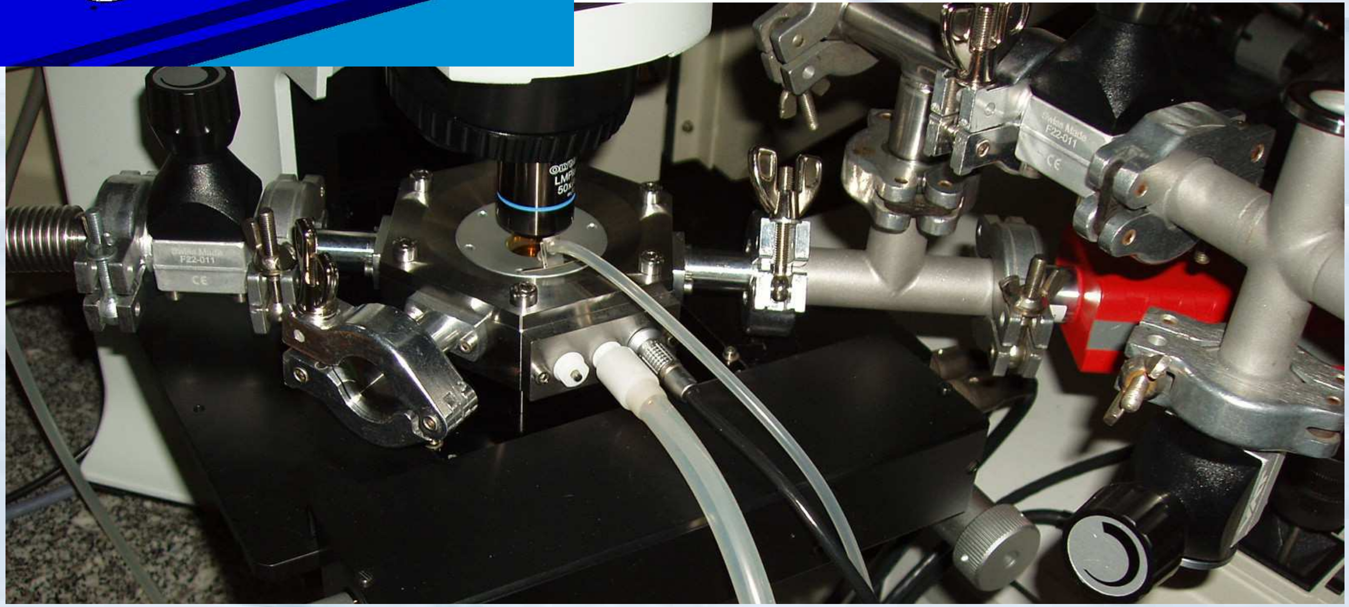


Nouveau Dispositif expérimental



Cellule Linkam

Gamme de T°: 77 K – 400 K (extensible à 10 K)
Rampe jusqu'à: 130 K /min
Stabilité < 0.1 K
Surface de l'échantillon ~ 22 mm
Vide limite: 2. 10-7 mbar
Résistance en platine
Echangeur: inox / cuivre
4 + 1 ports d'entrée / spectromètre de masse

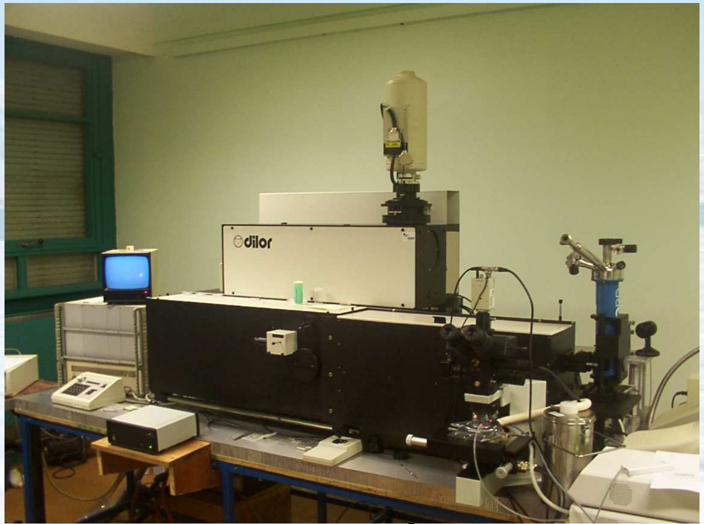


Dispositif expérimental

Spectromètre T64000

Focale: 640 mm

Collaboration avec Y. Guinet (LDSMM)



Focale: 800 mm
Réseaux:1800 traits/mm
Fente d'entrée: 200 µm
Puissance laser à l'échantillon: ~ 5 mW @ 514.5 nm

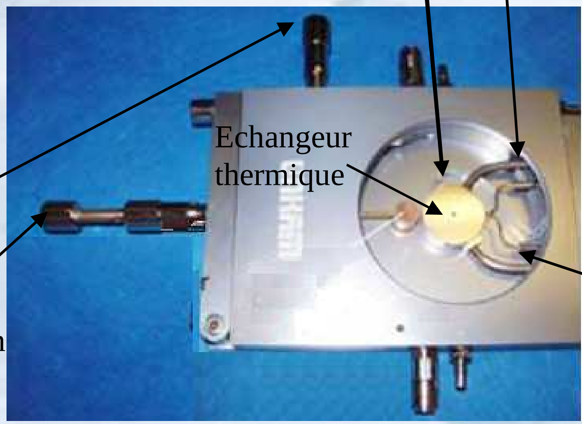
Spectromètre XY-Dilor

Circuit d'azote liquide

Capteur de température PT100

Echangeur thermique

Bras de manœuvre du porte échantillon



Connection électrique pour le chauffage

Gamme de T°: 77 K – 400 K
Rampe jusqu'à: 130 K /min
Stabilité < 0.1 K
Surface de l'échantillon 22 mm
Vide limite: 10^{-3} mbar
Résistance en platine
Echangeur en argent

Cellule Linkam FDCS 196

Neige

Milieu multiphasique complexe: air, glace, aérosols

Milieu idéal pour la détection des interactions gaz-glace:

- Glace/air plus favorable que nuages
- Accès facile
- Echantillonnage et mesures plus aisées
- Processus semblables à ceux des nuages