Diffusion of methane on amorphous solid water

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IEM

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Introduction

Icy mantles covering dust grains in dense clouds of the interstellar medium are known to be responsible for the large molecular complexity of the universe. Within those mantles atoms and molecules can meet and react with larger probability than in gas phase. In most cases, the chemical reactivity of interstellar ice is limited by the diffusion of reacting atoms or molecules in water ice, its major component. For this reason the knowledge of diffusion coefficients of different molecules in water ice is of great astrophysical interest [1].

In this work we have determined the surface diffusion of CH_4 in amorphous water ice, following an experimental procedure inspired in references [2, 3].

Experimental setup and methodology
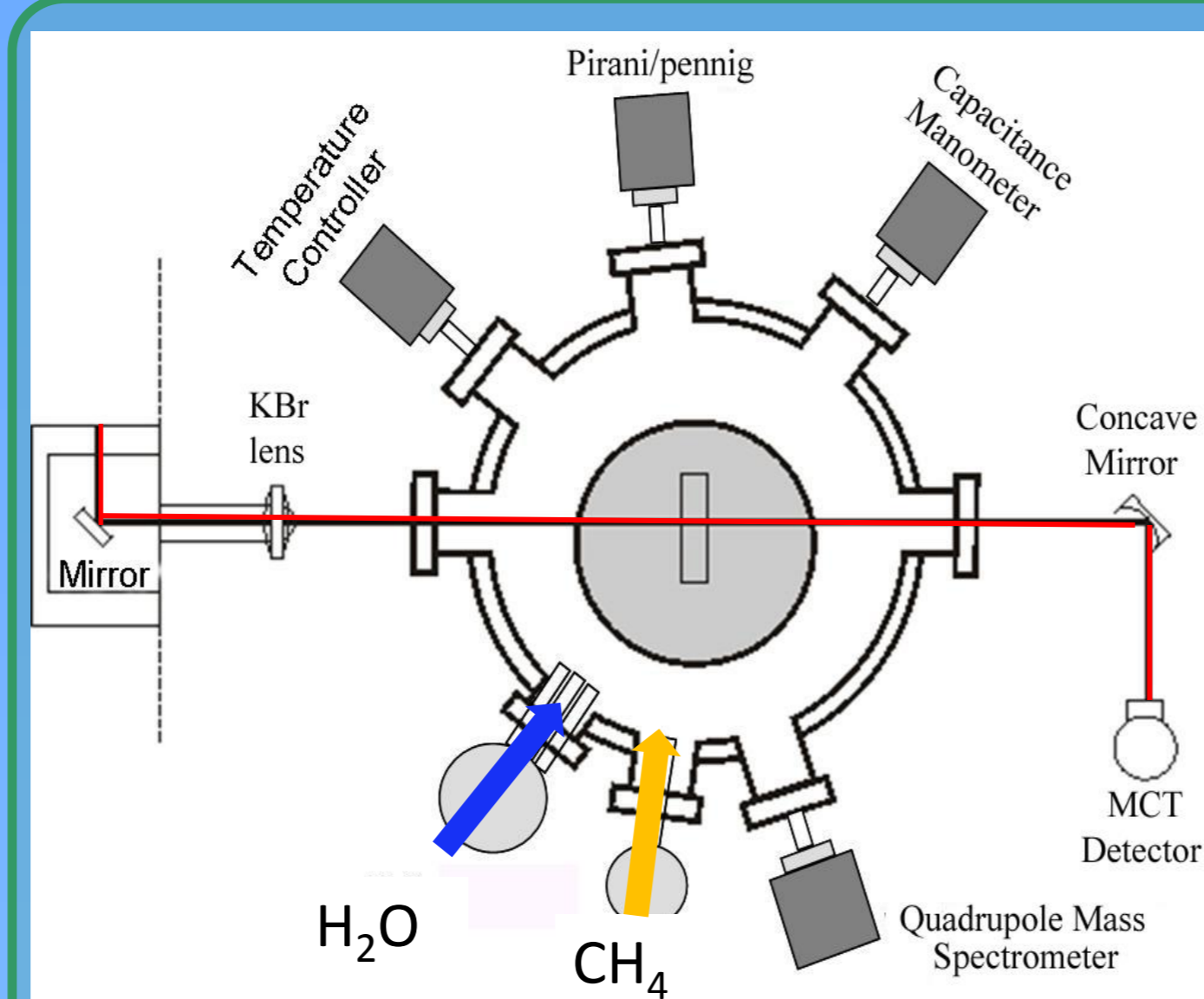
- High vacuum chamber: 10^{-8} mbar.
- Closed cycle He cryostat. 14-300 K
- Vertex 70 FTIR spectrometer.
- Quadrupole mass spectrometer

Experimental procedure:
In a high vacuum chamber methane ice layers covered by water ice layers were grown by vapor deposition at 30 K. Then, the CH_4:H_2O system was warmed at a controlled rate to 50 K and kept at that temperature while the diffusion of CH_4 molecules was monitored by means of FTIR spectroscopy. The decay of intensity with time of the strong IR absorption associated to the ν_3 mode of methane is a measure of the number of methane molecules that have moved through the pores of the amorphous water ice layer and left the sample.

Different experiments varying ice thicknesses, heating rates, and growing configurations (secuential or codeposited) were conducted.

Diffusion coefficients were extracted from the isothermal experiments using Fick's second law of diffusion [2,3].

CH_4/H_2O ice grown by **sequential deposition** at 30 K and warmed to 50 K

CH_4:H_2O ice grown by **codeposition** at 30 K and warmed to 50 K
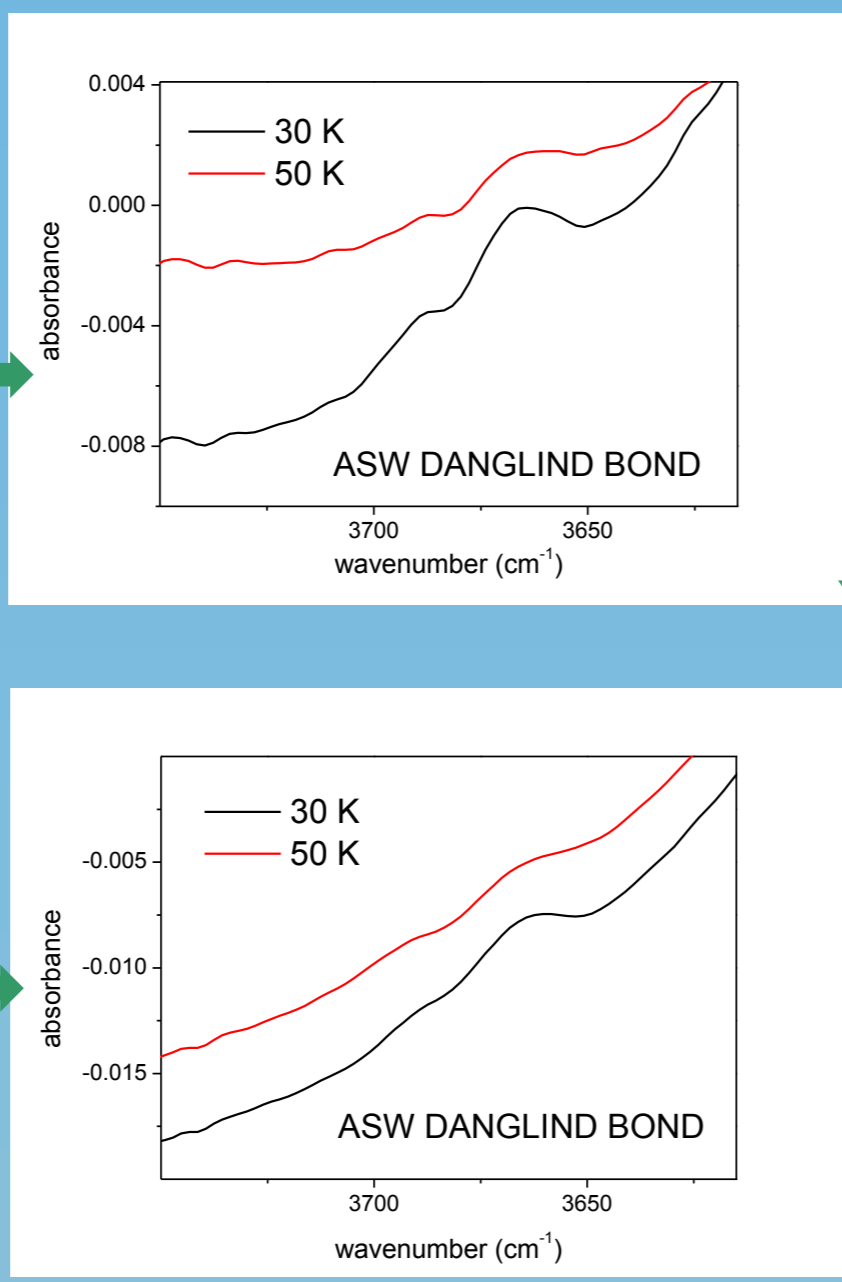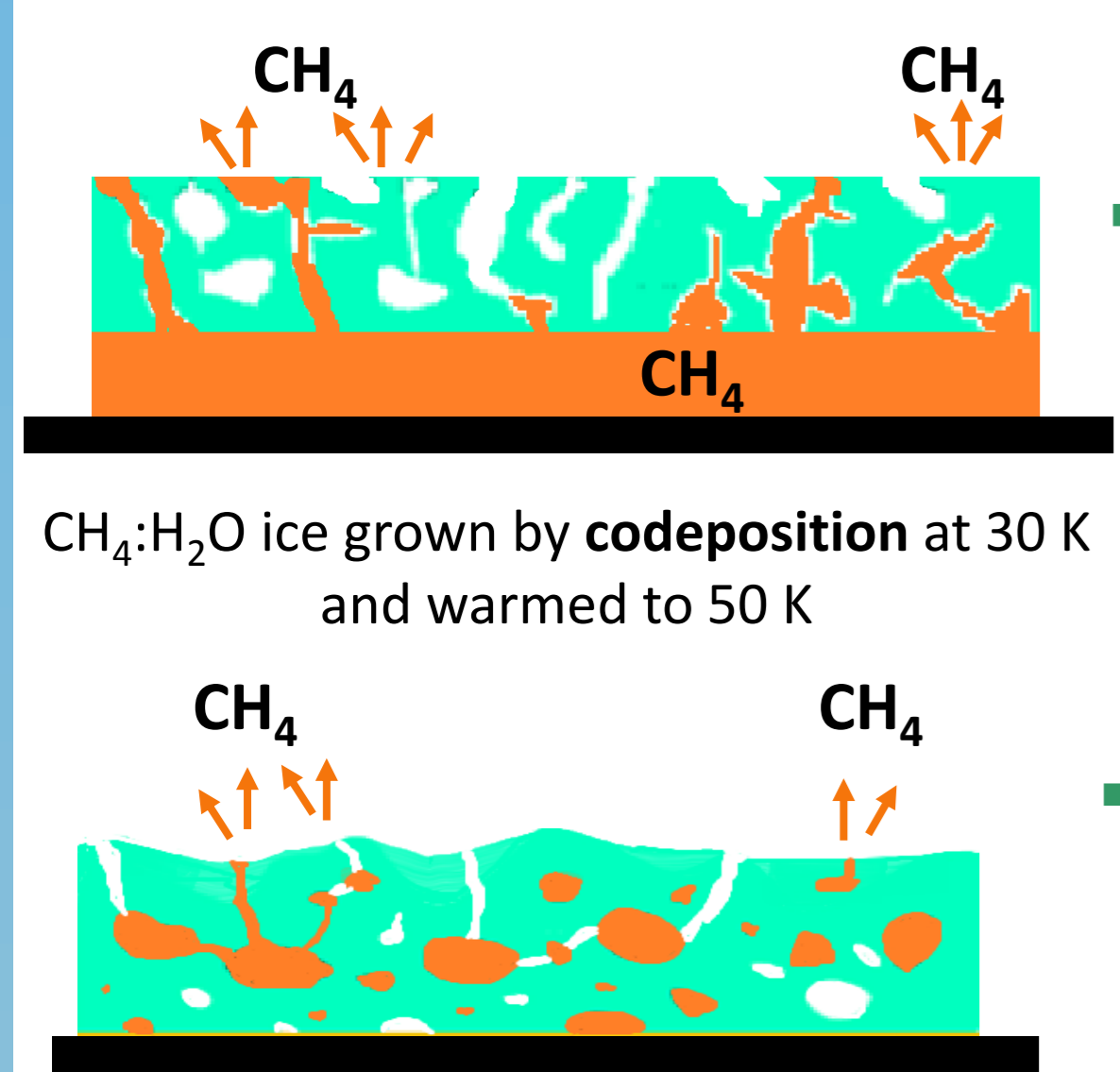
Mid-IR spectra of pure methane and a H_2O:CH_4 ice at 30 K
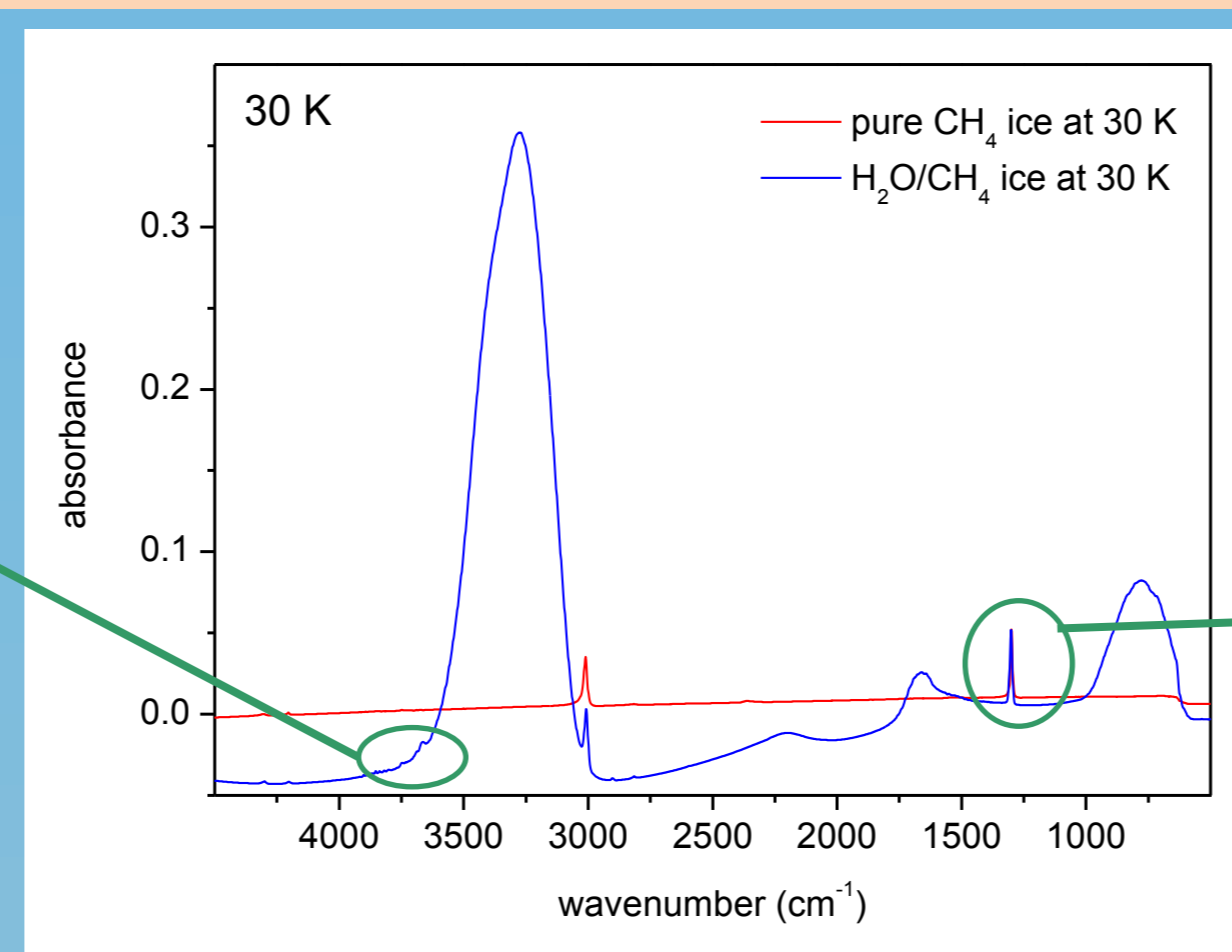

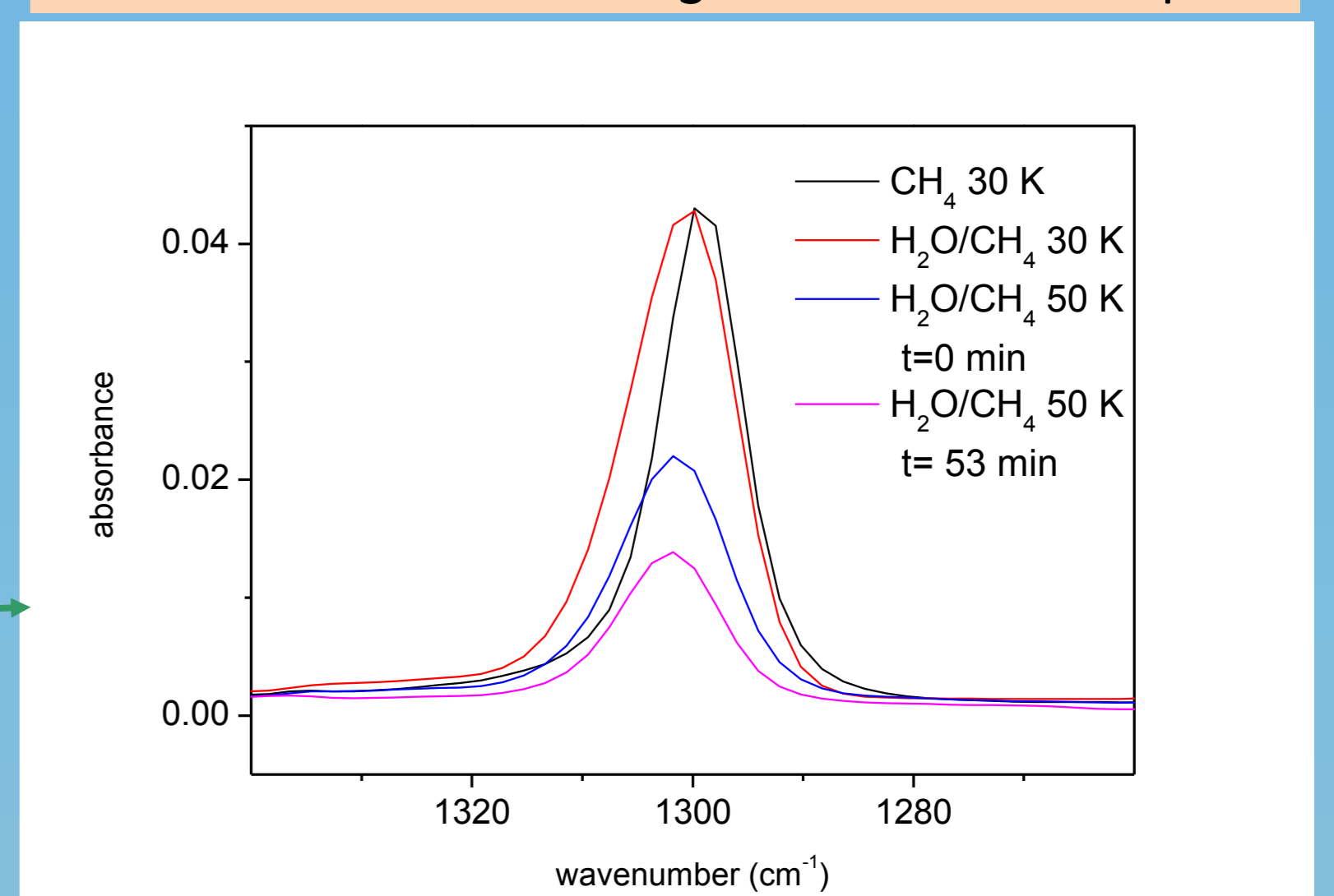Figure 2. Water ice deposited at 30 K is amorphous and porous (ASW).

## Evolution of the ν_3 mode of CH_4

Table of experiments

Exp.	T(K)	Config.	Heating rate	L_{H2O} (nm)	L_{CH4} (nm)	D x 10^{13} (cm²/s⁻¹)
1	50	secuential	5k/min	392	42	1.50 ± 0.5
2	50	secuential	5k/min	220	45	1.46 ± 0.5
3	50	secuential	20K/min	357	45	0.9 ± 0.5
4	50	secuential	5k/min	220	16	2.05 ± 0.5
5	50	secuential	10k/min	424	38	1.54 ± 0.5
6	50	secuential	10k/min	408	20	1.45 ± 0.5
7	50	secuential	5k/min	479	36	1.55 ± 0.5
8	50	codeposit.	5k/min	209	32	1.56 ± 0.5
9	50	codeposit.	10k/min	185	33	1.55 ± 0.5
10	50	codeposit.	5k/min	201	34	1.56 ± 0.5
11	60	secuential	5k/min	469	37	11 ± 10
12	60	codeposit.	5k/min	490	38	

Preliminary results

Intensity decay of the ν_3 mode of CH_4 versus elapsed time at 50 K.
Black dots: experimental.
Red line: fit to the Fick's model.
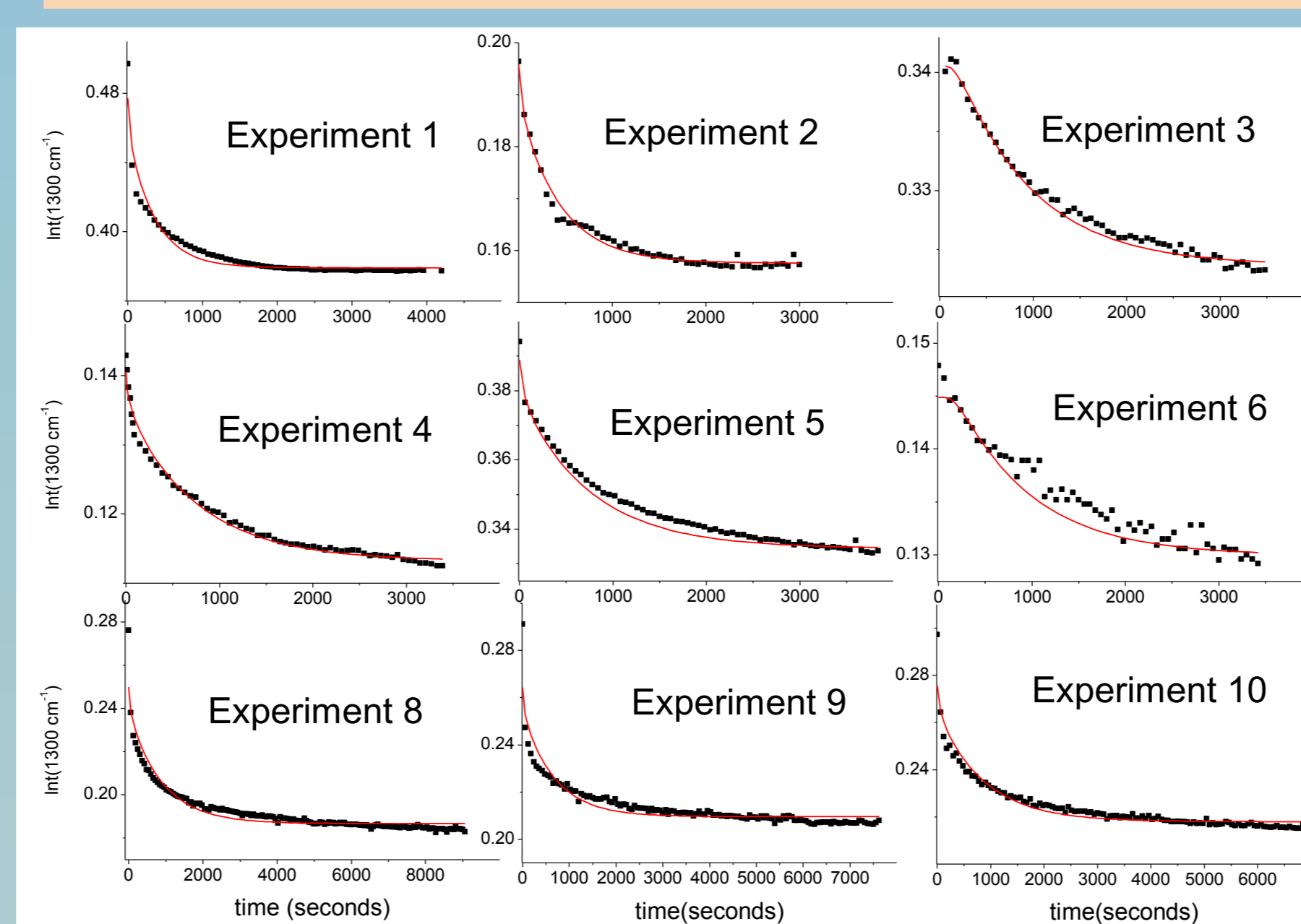
Fick's second law of diffusion

The concentration profile of CH_4, $c(x,t)$, in the ice can be described using Fick's second law of diffusion in one dimension:

$$\frac{\partial c(x,t)}{\partial t} = D(T) \times \frac{\partial^2 c(x,t)}{\partial x^2}$$

Where $D(T)$ is the temperature dependent diffusion coefficient.
It is assumed that D is constant with time. The rate of change in concentration with time is proportional to the rate at which the concentration gradient changes with distance in a given direction.

We take the initial conditions:

x= h → $c(h,t)=0$ — The molecules that reach the surface

x=0 → $\frac{\partial c(0,t)}{\partial x} = 0$. — No CH_4 can escape from the bottom of the film.

$c(x,0) = n_0$. If $0 < x < h$.

CH_4 homogeneously distributed in the ice at t=0, 50 K

Conclusions

➢ The diffusion of CH_4 molecules through ASW can be modeled with a Fick's second law of diffusion, with the contour conditions adequate to our experimental configuration.
➢ The different experimental conditions tested to modify water ice morphology gave diffusion coefficients for CH_4 at 50 K that vary 70% between them.
➢ At 50 K, methane diffuses about fifteen times slower than CO in amorphous water ice.

➢ *Methodology limitations*:
➢ a) the diffusion of molecules through amorphous solid water pores depends on water ice morphology, that is affected by the growing and annealing conditions of the ice;
➢ b) The temperature of study is limited to a small interval, above methane sublimation but low enough to be able to follow the diffusion with time.

Comparison with other works

Molecule	T(K)	D (cm² s⁻¹)	Reference
CH_4	50	1.5 ± 1 x 10^{-13}	This work
CH_4	60	1 ± 1 x 10^{-12}	This work
CO	40	5.1 x 10^{-13}	Karssemeijer [3]
CO	50	2.4 x 10^{-12}	Karssemeijer [3]
CO	40	8.0 x 10^{-13}	Mispelaer [2]
NH_3	115	4.5 x 10^{-13}	Mispelaer [2]
H_2CO	110	2.0 x 10^{-14}	Mispelaer [2]

References
[1] T.Hama-and N. Watanabe, *Chem. Rev.,***113**,8786-8839, 2013
[2] F. Mispelaer et al., *A&A,* **555***, A13,* 2013.
[3] L. J. Karssemeijer, *ApJ*, **781:16** (15pp), 2014.