METHANE DIFFUSION IN WATER ICE: RELEVANCE IN THE SOLAR SYSTEM

B. Maté [1], G. Molpeceres[1], J. Ortigoso[1], R. Escribano[1], I. Tanarro[1], V.J. Herrero[1], M. Domingo[2], R. Luna[2], C. Millán[2], C. Santonja[2], M.Á. Satorre [2]

(1) Instituto de Estructura de la Materia, IEM-CSIC, Serrano 123, 28006 Madrid, Spain. belen.mate@csic.es
(2) Centro de Tecnologías Físicas, Universitat Politècnica de València. Placeta Ferrándiz-Carbonell, s/n, 03801 Alcoi, Alicante (Spain). msatorre@fis.upv.es

Abstract

This work studies experimentally the diffusion of methane through water ice at astronomical relevant compositions and temperatures, by means of IR spectroscopy. Diffusion coefficients of methane on water ice are obtained applying the Fick's second law of diffusion.

To extend this study in the future to non-IR active molecules (i.e. N_2, O_2), a different experimental methodology, based on a cryogenic microbalance (QCMB) and laser interferometry (DLI) has been applied. The capacities of this novel approach has been tested comparing the results of methane diffusion.

1. Introduction

Water ice is the main component on the icy surface of some Solar Systems objects, like Europa [1] or Enceladus [2]. In other objects it is one of their icy components, like in comets [3], satellites like Triton [4], or TNOs such as Pluto [5].

Solid-gas phase equilibrium on these objects depends on different parameters: temperature, pressure, ice porosity, and desorption energy or diffusion of the volatile species from/through minerals or ices. Therefore, to understand the interactions between icy species is crucial for the comprehension of the processes occurring on these objects.

Methane-water mixtures are an appealing target, not only because they are present in most of the mentioned astronomical scenarios, but also due to its relevance in Earth's ice.

The methane-water diffusion coefficients obtained have been tested comparing two complementary experimental techniques at different laboratories.

2. Experimental

Methane/water dominated mixtures were background deposited at 30 K in two high vacuum chambers (Maté et al. [6]; Satorre et al. [7]). Ice mixtures were warmed with different ramps to temperatures relevant for Outer Solar System bodies (40-50 K). Methane lost was monitored at 50 K with IR spectroscopy, or with a QCMB and DLI at 40, 41, 42, 44, 46 K (see Fig. 1). Fig 1 top panel shows the 1300 cm^{-1} CH_4 infrared absorption band chosen to monitor the CH_4 loss. The central panel displays the evolution of the area of this band, as methane sublimate form water ice, versus time elapsed at 50 K. An exponential decay is observed. The same behavior is also observed with the QCMB, considering that any oscillator increases its frequency (right axis Fig. 1 bottom) with mass lost.

3. Simulations

To deduce the diffusion coefficient, the second Fick's diffusion law (Eq. 1) was employed.

$$A_h(t) = s + \sum_{i=1}^{\infty} \frac{2(A_o - s)}{\mu_i^2 h^2} e^{-\mu_i^2 D t} \qquad (1)$$

Where $A_h(t)$ is the bands area, s is an offset, A_o is the band's area at t = 0 s, $\mu_i = (2i+1)\pi/2 \cdot h$, where i =1, 2, 3… is an integer and h the ice layer thickness, D is the diffusion coefficient, and t is the time in s. This model assumes the following approximations: methane molecules are homogenously distributed in the ice film; methane molecules move through static water ice structure; methane molecules move unidirectionally forward to the ice surface; no methane molecules moves backward; all the molecules arriving the surface sublimate immediately.

The model was modified to describe layered samples (methane ice covered by water ice), offering the same results than co-deposited samples.

Results obtained at 50 K are comparable with other published diffusion coefficients for CO, H_2CO and NH_3 in water ice [8, 9]. At 50 K the value obtained for CH_4 is about 15 times lower than that obtained by Karssemeijer et al. [9] for CO at 50 K, and only three times lower than that obtained by the same author for CO at 40 K. These values must be taken into account only as a reference, because at temperatures higher that 38 K (up to around 70 K) water ice deposited at lower temperatures suffers a phase change from High Density to Low Density Amorphous Solid Water (HD-ASW to LD-ASW)[10]. The kinetics of this phase change depends on temperature, time and the initial structure of the ice formed. Because changing initial deposition conditions or warming up procedures can influence the diffusion value, to compare different results the structure of water must be considered.

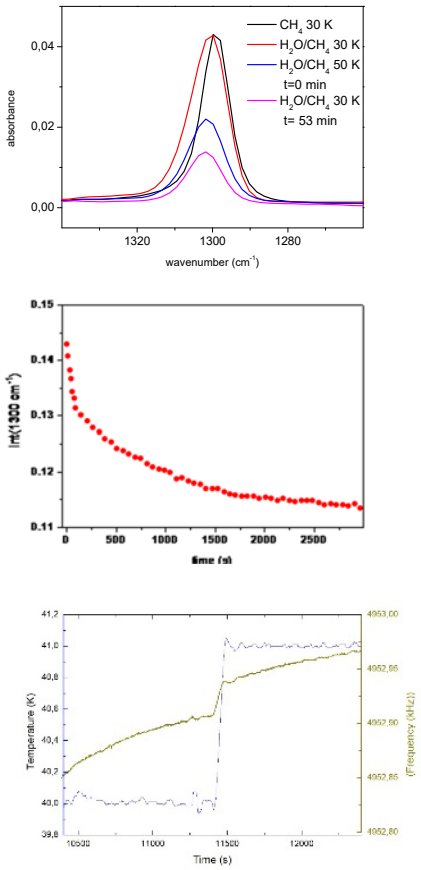

Figure 1. a) *Top panel. 1300 cm^{-1} absorption band for CH_4 ice at deposition temperature (30 K), and at the beginning and end of a diffusion experiment at 50 K.* ***b)*** *Central panel: evolution of the area of the 1300 cm^{-1} band with time at 50 K.* ***c)*** *Temperature (K) and QCMB (kHz) variation during desorption at 40 and 41 K.*

4. Conclusions

Methane diffusion through amorphous solid water (ASW) can be modelled by the Fick's second law of diffusion.

ASW changes from high density to low density at temperatures relevant to the Outer Solar System (approx. 40-70 K). These structural modifications affect the diffusion of methane molecules through it.

Structural changes can be studied by means of laser interferometry, simultaneously with IR or QCMB, to obtain the diffusion coefficient and unveil its relationship with the structure.

At 50 K the diffusion coefficient of CH_4 measured (by FTIR) is about 15 times lower than that of CO.

CH_4 diffuses about 7 times faster at 60 K than at 50 K.

References

[1] Fanale, F. P. et al. (1999) Icarus, 139, 179–188

[2] J. Hunter Waite Jr., et al. (2006) Science, 311, Issue 5766, pp. 1419-1422

[3] Bockelée-Morvan D. et al. (2016) MNRAS, 462, S170–S183

[4] Quirico E. et al. (1999) Icarus, 139, 159–178

[5] Protopapa S. et al. (2017) Icarus, 287, 218-228

[6] Maté et al. (2017) MNRAS, 470, 4222–4230

[7] Satorre et al. (2018) Laboratory astrophysics. (pp. 51-69) Ed. Guillermo M. Muñoz-Caro and Rafael Escribano, Astrophysics and Space Science Library. Springer.

[8] Mispelaer et al. A&A, 2013, 555, A13 (11 pp)

[9] Karssemeijer et al. ApJ, 2014, 781:16 (15 pp)

[10] Jenniskens, P. and Blake D. (1994) Science, 295, 753-756