



Formation of gas hydrates from vapour deposition of nitrogen and water: an in-situ study by Raman spectroscopy

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Gas hydrates possess a potential for useful applications in many technical and industrial applications in the fields of energy and environmental research [1]. They can be found in a variety of natural environments such as hydrate-bearing marine sediments, the permafrost or even atmospheric aerosols [2]. Nitrogen-bearing clathrates occur naturally on Earth where they form small crystals of air-clathrates embedded in the ice matrix in polar ice core [3]. They are potentially astrophysical players in the formation of nebulae [4], comets [5] and of outer solar system planets [6]. For instance, Enceladus is expected to feature a combination of conditions favourable to clathrate production with the availability of large quantities of water, low temperature in the interior or at the surface, and a large pressure gradient from the surface to the interior of the planet. Therefore, a large amount of gas species (such as N₂, CO, CO₂, etc.) might be trapped in clathrate forms either during vapour re-deposition after gas plume ejections at the pole or within a high pressure-low-temperature environment such as that found within the ocean of the planet interior. Trapping of gases in clathrates might also explain the possible noble gas de[U+FB01]iciencies detected in planetary environments [7].

In this work, in-situ micro-Raman spectroscopy, adapted to investigate gas hydrate [8], is used to study the formation of clathrates from thin films obtained by vapour deposition of nitrogen and water vapor at low pressure (10⁻² – 10³ mbar) and low temperature (77-200K). Sequential deposition consists in the condensation of (a) H₂O and then (b) N₂. An amorphous thick ice film (amorphous solid water) is first observed at 80K and characterized spectroscopically by Raman. Then nitrogen gas is injected into the sample chamber. During heating process (with 10 K increments), the amorphous film transforms into crystalline ice over a temperature range of 60 K. The nitrogen molecules are enclosed in the amorphous porous ice structure and become engaged into a N₂-clathrate structure above 150K, revealed by the Raman signatures of guest partitioning in the water cages as evidenced in the nitrogen hydrate [9]. Co-deposition consists in the simultaneous deposition of nitrogen and water vapor at some specific gas-mixing ratio and temperature conditions of 80K. In this case, no clathrates could be observed and most N₂ trapped initially into ASW is released during ice crystallization.

[1] E.D. Sloan, *Nature*, 426, 353-363, (2003)

[2] E.D. Sloan, C.A. Koh, 3rd ed.; Taylor & Francis-CRC Press: Boca Raton, FL, (2008)

[3] H. Shoji, C.C.Jr. Langway, *Nature* 298, 548-550, (1982)

[4] F. Hersant et al., *Astrophys. J.*, 554, 391-407, (2001)

[5] S. Lectez et al., *Astrophys. J. Lett.*, 805 : L1 (4pp), (2015)

[6] A. Bouquet et al., *Geophysical Res. Lett.*, 42, 1334–1339, (2015)

[7] O. Mousis et al., *Astrophys. J. Lett.*, 740, L9, (2011)

[8] B. Chazallon et al., *Gas Hydrates: Fundamentals, Characterization and Modeling*: D. Broseta et al., Eds.; Wiley-ISTE: London, Vol. 1, pp 63–112, (2017)

[9] C. Petuya et al., *J. Phys. Chem. C* 2017, ASAP.