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Clathrate Hydrates

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Low-Pressure Synthesis and Characterization of Hydrogen-Filled Ice Ic**

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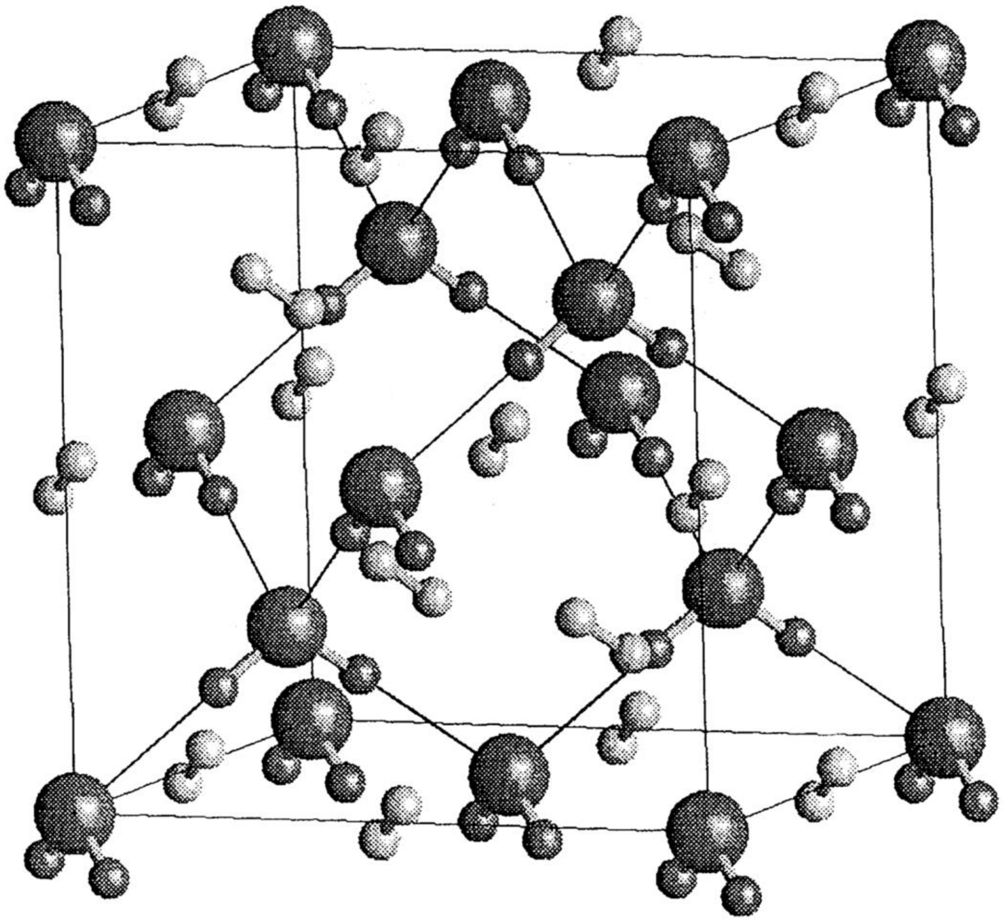
Overview of the work

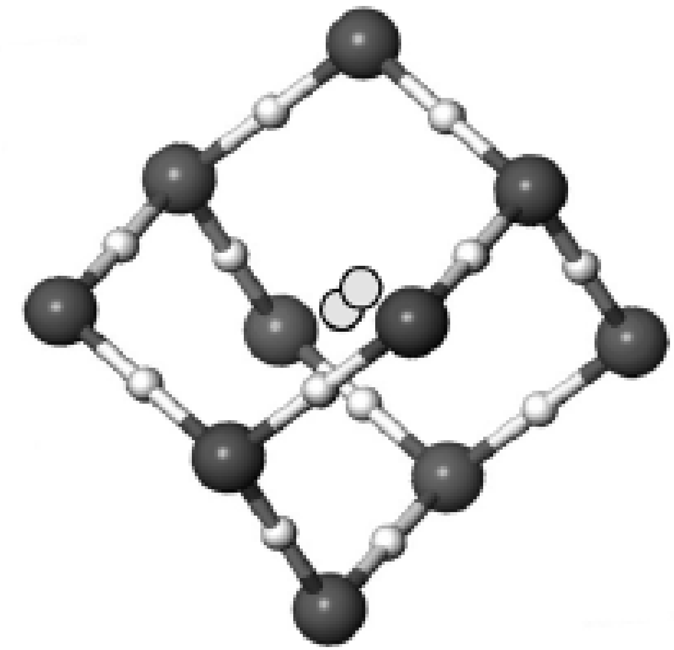
1. In this paper, they have demonstrated that amorphous ice plus hydrogen gas can be converted to an ice Ic framework partially filled with H_2 (designated as H_2:H_2O-Ic), by annealing at pressures less than 18 MPa.
2. From calculations, they have suggested that it may be possible to prepare 50% filled H_2:H_2O-Ic (5.3 wt% H_2) at pressures below 45 MPa.
3. This material may be closely related to the C_2 phase of Ice which is similar to Ice Ic structure and could have broad implications for hydrogen storage and also astrophysics.
4. Indeed it may be present in our solar system and elsewhere, wherever vapour deposition and annealing are common processes.

Background

Ice Ic = Cubic Ice
Ice Ih = Hexagonal Ice



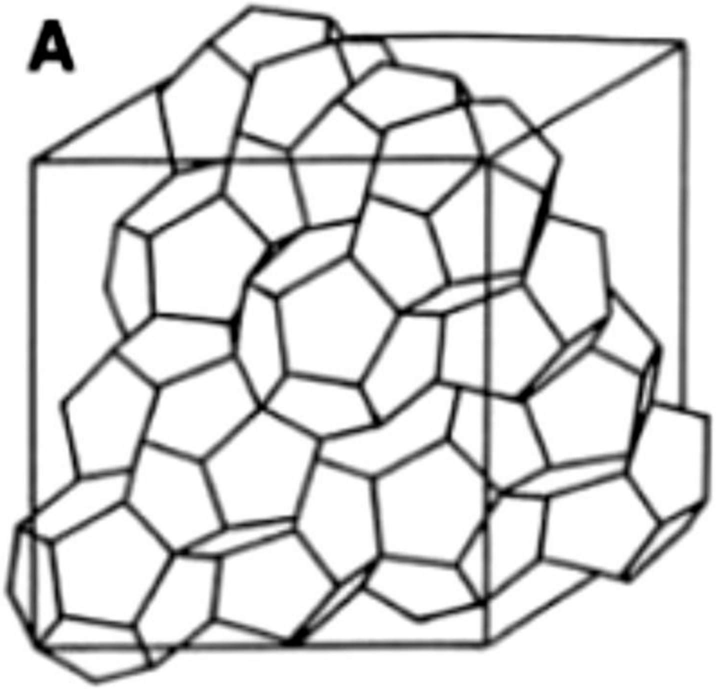
Crystal structure of cubic hydrate (C_2 phase), ice Ic



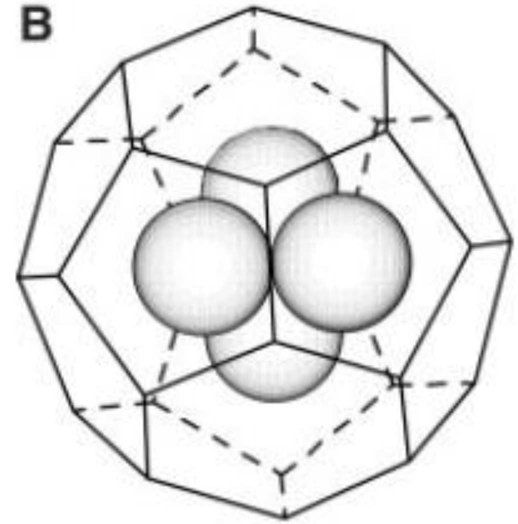
Adamentane shape cavity

W. L. Vos, L. W. Finger, R. J. Hemley, H. K. Mao, *Phys. Rev. Lett.* **1993**, 71, 3150.

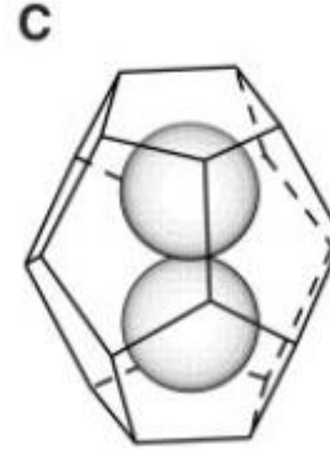
Background



A. The sII crystal structure consisting of $5^{12}6^4$ and 5^{12} building blocks



B. A tetrahedral cluster of four hydrogen molecules in the $5^{12}6^4$ cage.

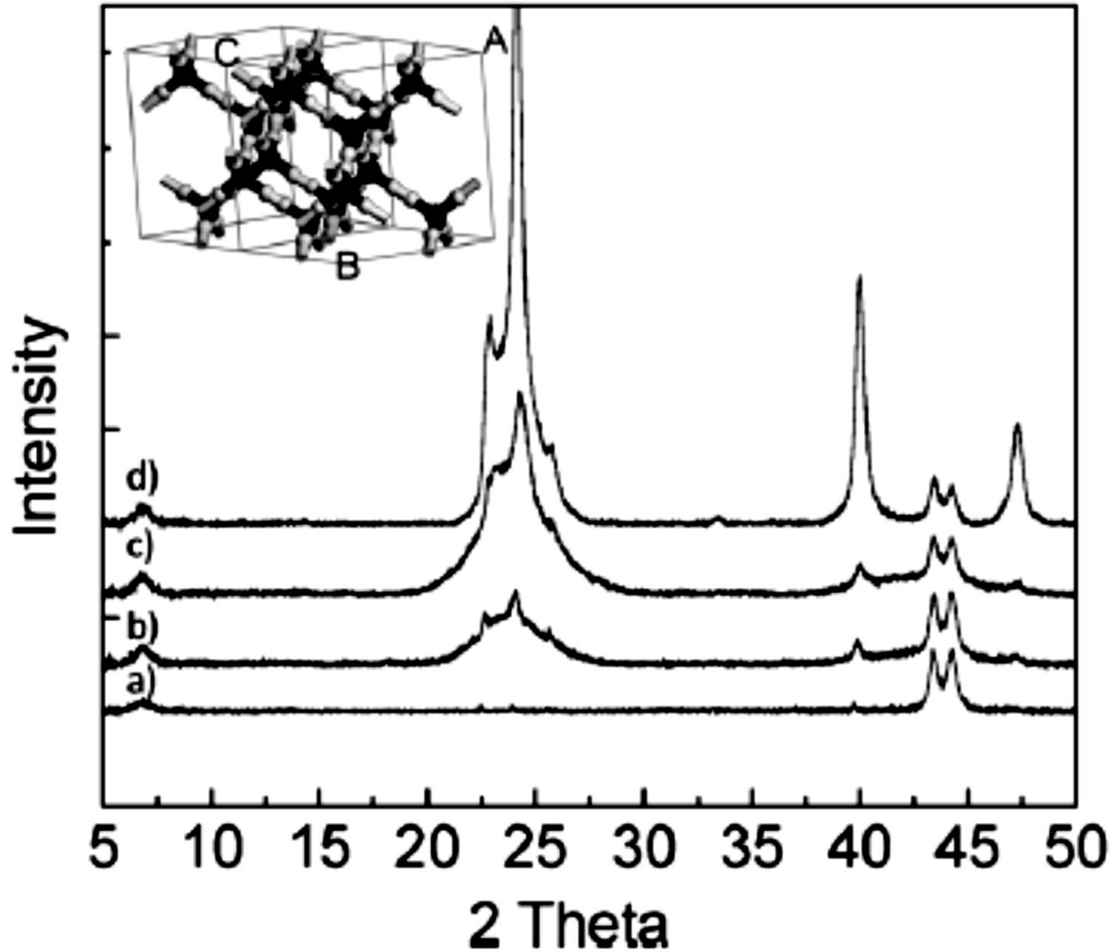


C. A cluster of two hydrogen molecules oriented toward opposite pentagonal faces in the 5^{12} cage.

W. L. Mao, H. K. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Guo, J. Hu, J. Shu, R. J. Hemley, M. Somayazulu, Y. Zhao, *Science* **2002**, 297, 2247 – 2249

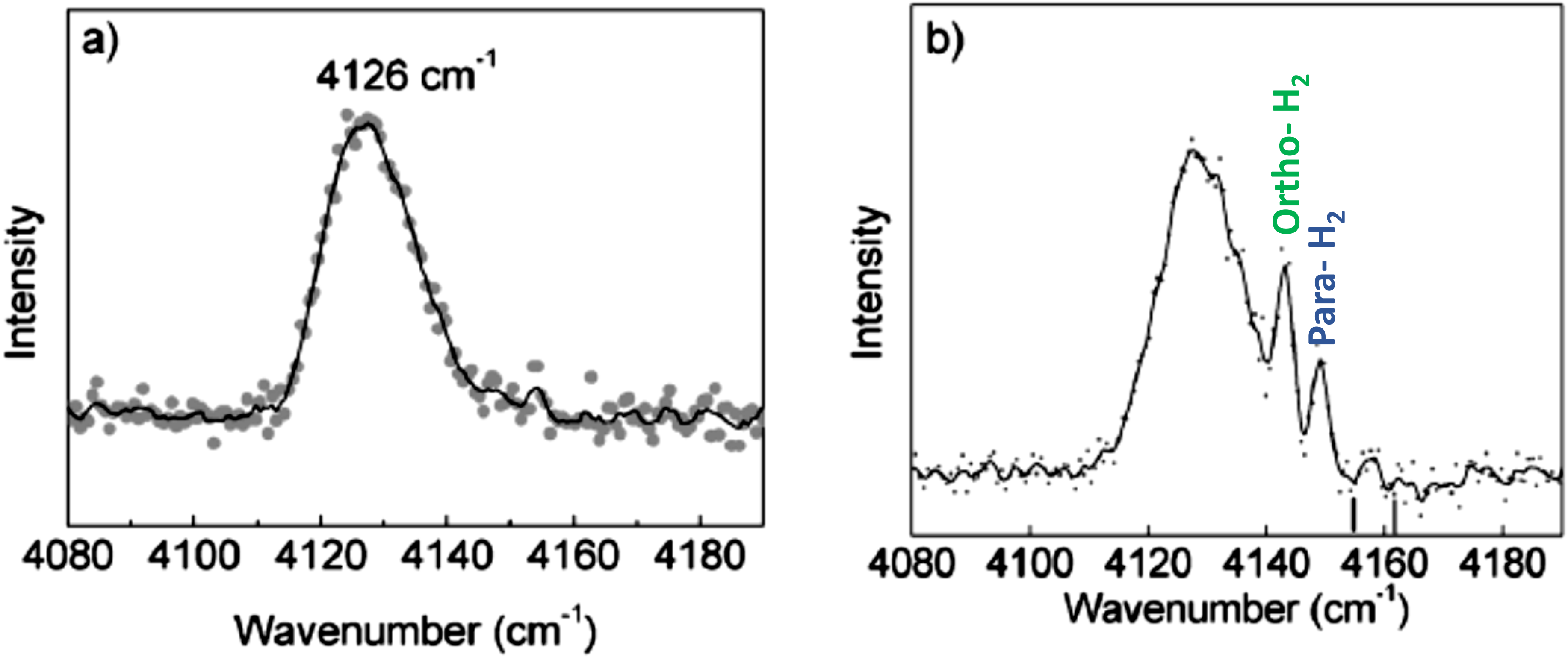
Experimental method

1. Amorphous H_2O and D_2O ices were prepared by vapour deposition of water vapour onto a cold copper plate in a vacuum chamber on the evacuated tail of a closed cycle helium cryostat maintained at 15 K.
2. Samples were then removed at 77 K and stored in liquid nitrogen until used for further sample characterization and subsequent sample preparations.
3. The amorphous ice was placed in high-pressure Swagelok stainless steel vessels cooled with liquid nitrogen which were then warmed to 80 K and evacuated to remove residual nitrogen gas.
4. The vessel was then filled with cold hydrogen or deuterium gas at typically between 8–18 MPa pressure and the amorphous ice plus hydrogen was then annealed to temperatures in the range 135–160 K.
5. After annealing, samples were re-cooled to 77 K, removed from the pressure vessel and maintained at 77 K for further characterization.



Powder X-ray diffraction data for amorphous ice and annealed amorphous ice

a) Sample holder, b) amorphous ice from vapor deposition at 15 K, stored in liquid nitrogen and analyzed at 120 K, showing traces of ice Ic and ice Ih. c) Sample prepared from amorphous ice with 15 MPa H_2 and 140 K annealing, then analyzed at 130 K, showing a mixture of ice Ic, and amorphous ice. d) Ice Ic sample prepared from amorphous ice with 15 MPa H_2 and 150 K annealing, then analyzed at 130 K.

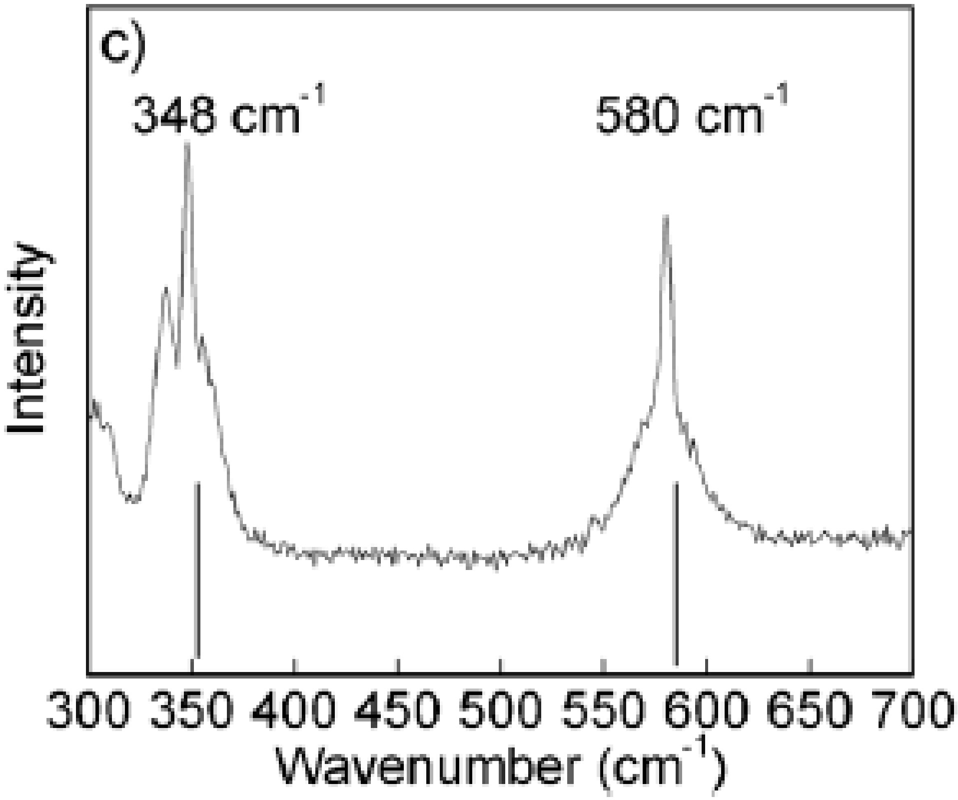


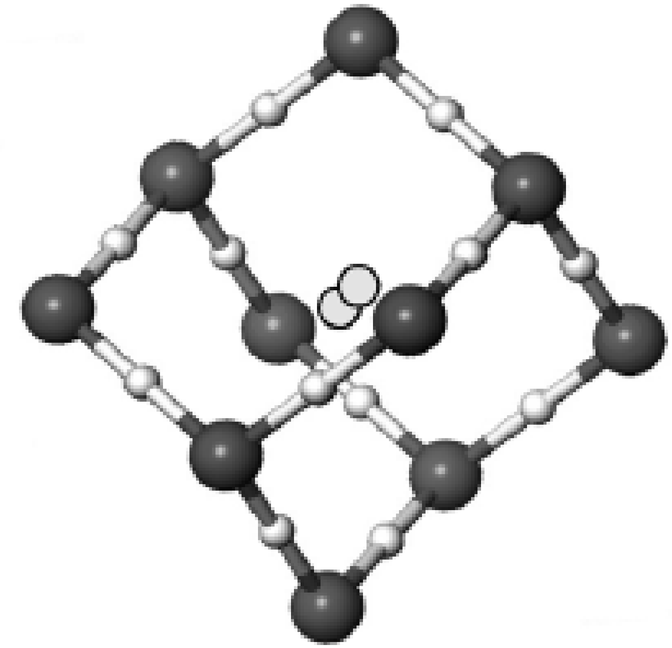
Raman spectra at ambient pressure and 77 K of samples prepared by annealing amorphous ice at 140 K exposed to H_2 at pressures of 15 or 18 MPa.

a) H_2 vibron band of H_2:H_2O-Ic. (Experimental)

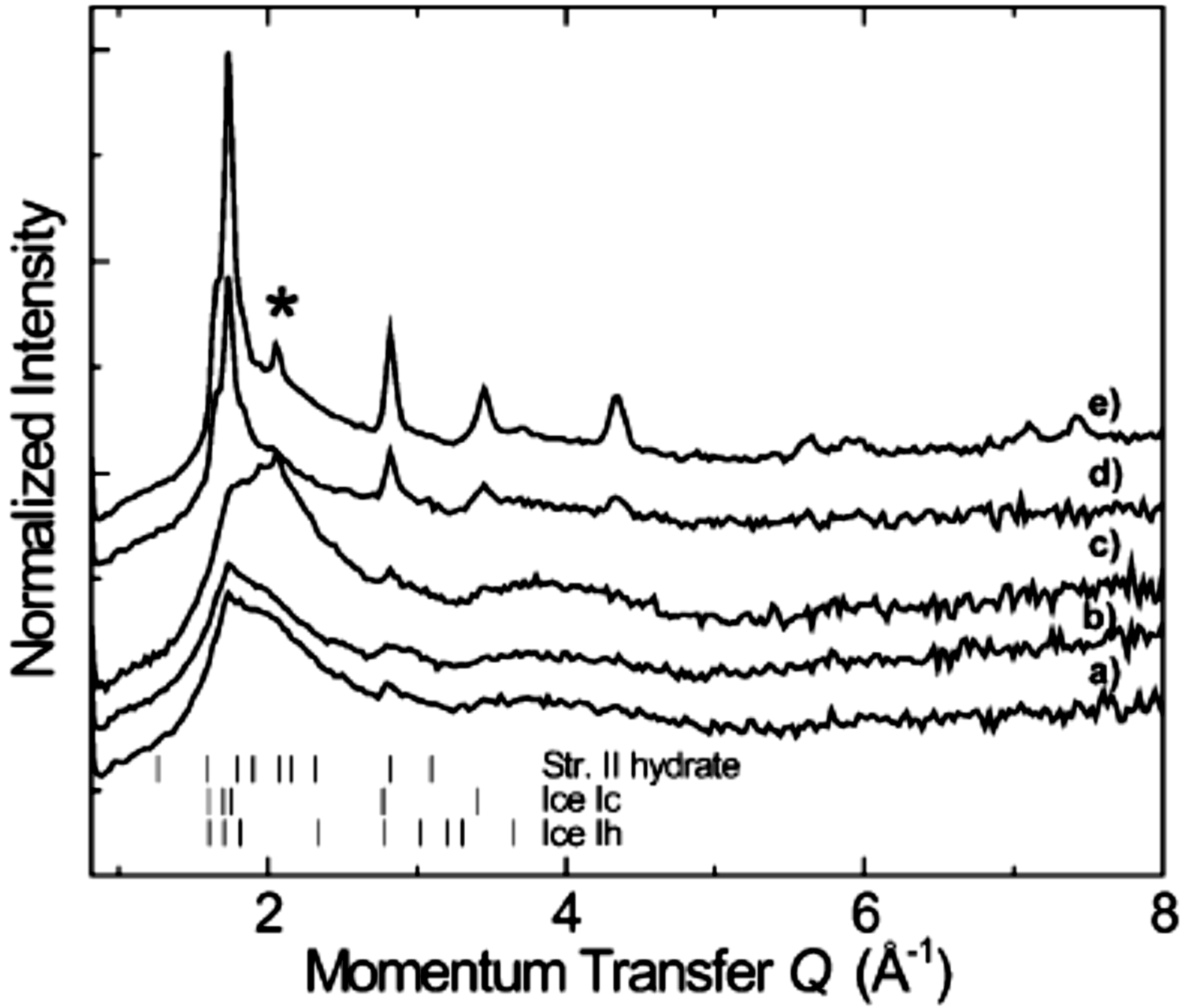
b) H_2 vibron band of H_2:H_2O-Ic showing additional sharp lines from H_2 Str. II clathrate hydrate and vertical lines for H_2 gas-phase vibron frequencies. (Ref)

B. P. Stoicheff, Can. J. Phys. 1957, 35, 730 – 741.

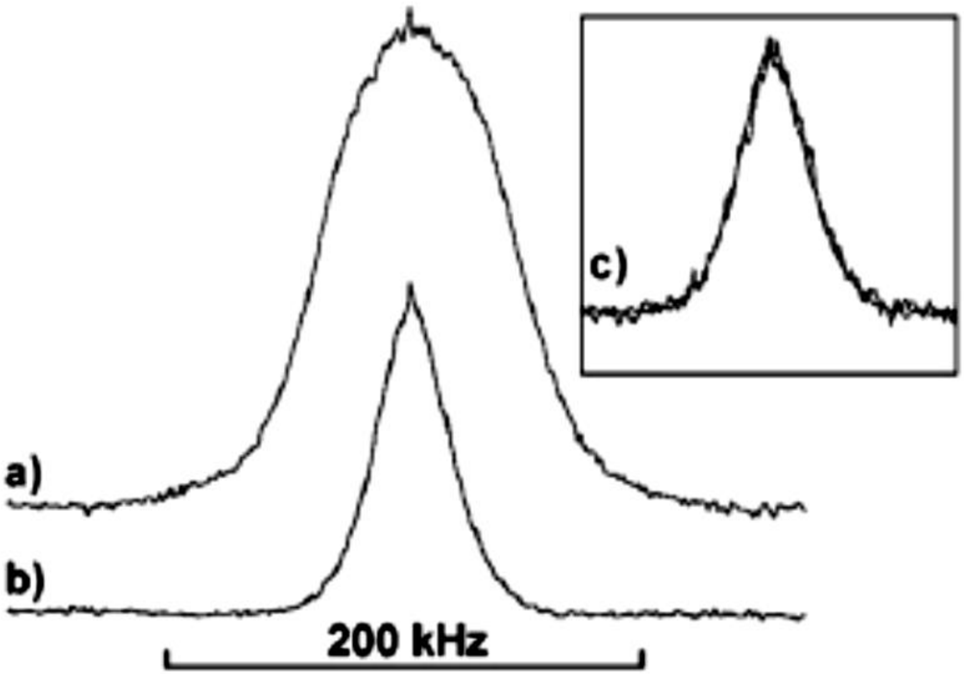




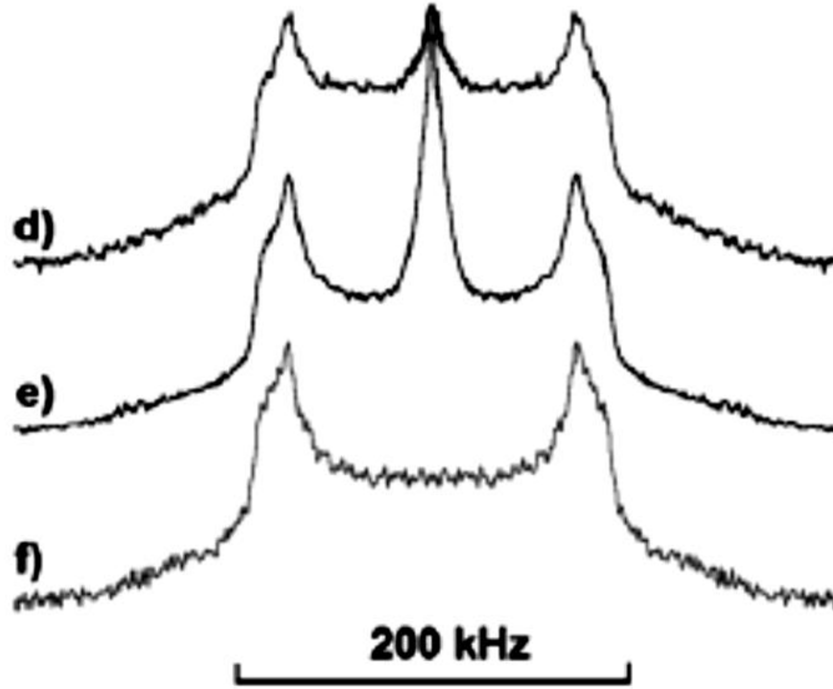
c) H_2 roton bands showing sharper H_2 Str. II clathrate hydrate lines superimposed on broader H_2:H_2O-Ic bands (para-H_2 band at lower frequency).
d) H_2 molecule at the center of an adamantane-shaped cavity in ice Ic.



In situ neutron diffraction data for annealing of amorphous ice under a D_2 gas pressure of 11.7 MPa, sequentially from bottom: a) not annealed, b) annealed at 140 K, c) quenched to 50 K, d) annealed at 150 K, and e) quenched to 50 K. The vertical lines identify the location of the features due to ice phases and Str. II clathrate hydrate. The dominant peak of the Str. II clathrate is indicated by the "*".



^1H NMR spectra (300 MHz) at 77 K: a) H_2:H_2O-Ic (prepared at 17.5 MPa, 150 K) and b) H_2:D_2O-Ic (13.5 MPa, 150 K). Recycle times of 1 s. Spectra scaled to show approximate relative intensities.
c) Two superimposed spectra of H_2:D_2O-Ic with different recycle times. 400 scans at 1 s per scan, 40 scans at 30 s per scan and scaled up by a factor of 10.



^2H NMR spectra (46.05 MHz) at 77 K: d,e) D_2:D_2O-Ic (16 MPa, 150 K), recycle times of 300 s and 8 s respectively.
f) D_2O amorphous ice after pressurizing with D_2 at 10 MPa, annealing at 110 K, and depressurizing at a recycle time of 300 s.

Total radial distribution function, G(R), for D_2O Ice-Ic

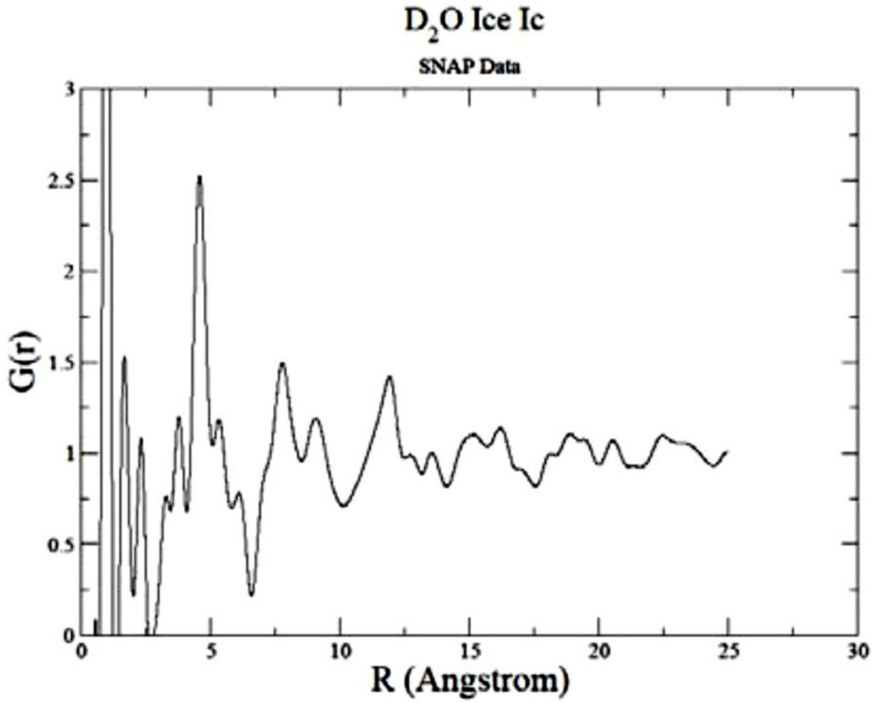


Fig. a

Fig. a Experimental G(R) from neutron diffraction data.

Fig. b G(R) obtained using the Faber Ziman formalism with partial G(R) components from MD simulations.

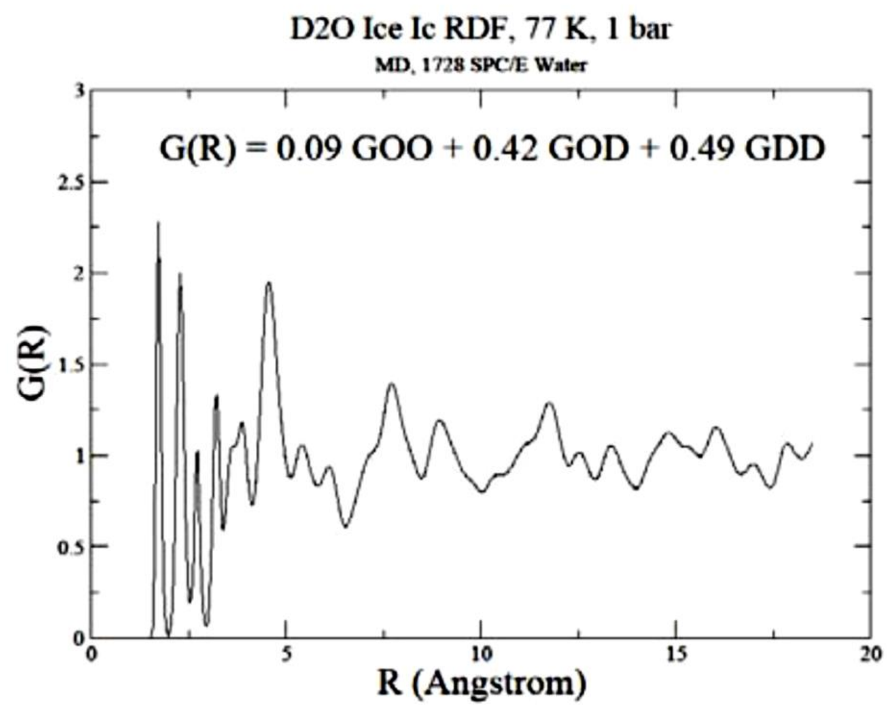


Fig. b

Summary

1. In summary, in this low-temperature approach a combination of factors results in the incorporation of H_2 into the ice Ic (or in some cases the Str. II clathrate hydrate) framework upon annealing.
2. The exceptional porosity of vapor-deposited amorphous ice allows intimate contact between ice and H_2 over a very large surface area throughout the material.
3. Moderate pressures make a high concentration of H_2 available right at the sites where reorganization of low-density amorphous ice into ice Ic occurs following the apparent glass transition at about 135 K, ensuring efficient H_2 incorporation into the ice Ic cavities..
4. The potentially large H_2 capacity of ice Ic (10 wt% if fully loaded) prepared by this route at moderate pressures suggests ice Ic could be a viable hydrogen storage material.

Thank You

Species	**Vibron Band (cm^{-1})**	**Reference**
H_2:H_2O-Ic	4126	This paper
Gaseous H_2	4155.2	Can. J. Phys. 1957, 35, 730 – 741.
H_2 in dense ice	4150	Chem. Phys. Lett. 1996, 257, 524 – 530
H_2 in ice Ih	4173	J. Chem. Phys. 1992, 96, 3367 – 3369