Experimental Report

13/01/2014

Proposal:	**5-25-217**	**Council:**	10/2012

Title: Touching the holy grail of gas hydrate research: The empty clathrate,a new crystalline form of ice

This proposal is a new proposal

Researh Area: Physics

Main proposer: **KUHS Werner Friedrich**

Experimental Team:
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Samples: D2O (and Ne*6D2O)

Instrument	Req. Days	All. Days	From	To
D20	3	5	11/03/2013	14/03/2013
			08/04/2013	09/04/2013
			03/07/2013	04/07/2013

Abstract:

A previous experiment (5-25-209) has allowed us to find a way to the empty clathrate hydrate structure, a phase of prime interest in gas hydrate research. This time we want to fully achieve this goal by pumping on Ne-hydrate and, in this way, form a new phase of ice which is topologically related to the so-called structure II clathrate hydrate; it is predicted theoretically as the most stable crystalline phase of water at negative pressures. This phase should have a negative thermal expansion, which we want to demonstrate experimentally by measuring its temperature-dependent lattice constant. We also plan to measure the emptying of the cages by pumping out the neon atoms in situ at various temperatures in order to elucidate the activation energy of the cage-to-cage migration of neon atoms in bulk hydrate.

The results of the experiment 5-25-217 have been submitted to Nature on December 23rd, 2013. Below a summary is given and some important figures of this submission are shown.

Formation and properties of an empty clathrate hydrate structure

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Author contributions: WFK and AF designed research; AF, TCH and WFK performed research; TCH and WFK analysed data; and WFK wrote the paper.

The hypothetical empty clathrate hydrate structure is the corner-stone of the statistical thermodynamic theory of gas hydrates on which our understanding of stability limits and composition of gas hydrates is based. We now have produced, for the first time, empty hydrate of structure sII and determined its crystal structure, thermal expansivity and stability limit. The empty hydrate can be considered as the seventeenth experimentally established crystalline ice phase and is predicted to be the stable low-temperature configuration of water at negative pressures. With a density of 0.81 g/cm^3 it is the least dense of all known crystalline phases of water. We succeeded preparing this new phase in a region of thermodynamic metastability by pumping on small spherical particles of Ne-clathrate at temperatures of ~ 140 K (see Fig.1). In contrast to the filled hydrates, and similar to ice Ih, the empty hydrate structure exhibits negative thermal expansion below ~ 55 K (see Fig.2 and 3), which is likely to be related to low-energy bending modes of the H-bonded water framework. Its lattice constants are larger than the ones of Ne-clathrate, demonstrating and quantifying the importance of attractive interactions of water and small gas molecules in clathrate hydrates. From these results a more balanced view of gas hydrates emerges: While the excluded volume effect upon guest inclusion stabilises mechanically the clathrate structure to higher temperatures, the guest-host interactions are quite sizeable for their energetic stabilization and lead to considerable changes of the density of the water framework.

A comparison of the empty and Ne-filled sII structure confirms and quantifies the importance of attractive guest-host interactions in clathrate hydrates. The interaction of the water host with Ne atoms leads to a volume reduction of 0.4% for the water frame at 5 K, which is a very substantial effect (Fig. 2). Effects of similar magnitude had indeed been predicted by lattice dynamical MD work. For the change in volume of the small 5^{12} cage, we obtain an even larger reduction of 0.5%. This is not captured at all by recent *ab initio* calculations for an isolated dodecahedral 5^{12} water cluster with and without Ne, for which identical volumes were found.

From our work emerges a more balanced view on gas hydrates and water-gas interactions in general. While the original statistical thermodynamic theory resorted to a Langmuir adsorption picture with a resulting energetic stabilization of the host-guest complex (albeit without changes of the structural framework), later work had shifted the emphasis to the excluded volume effect (“kinetic effect”) of hydrate stability. It is noteworthy in this context that a structure with sI clathrate hydrate topology is the best solution to the so-called Kelvin problem of maximizing the surface area with a given amount of water molecules, which in turn must mean that the water molecules like to interact with their hydrophobic guests as long as no H-bonds are sacrificed. All water clathrate topologies are the result of a systematic hydrophobic hydration of the encaged apolar guest molecules. Our experimental results clearly show that both kinetic and energetic contributions are important for stabilization; they should now be further quantified for a full understanding of gas hydrates, their stabilities and physical properties. The established empty hydrate water frame provides a computational as well as experimental reference for such future efforts.

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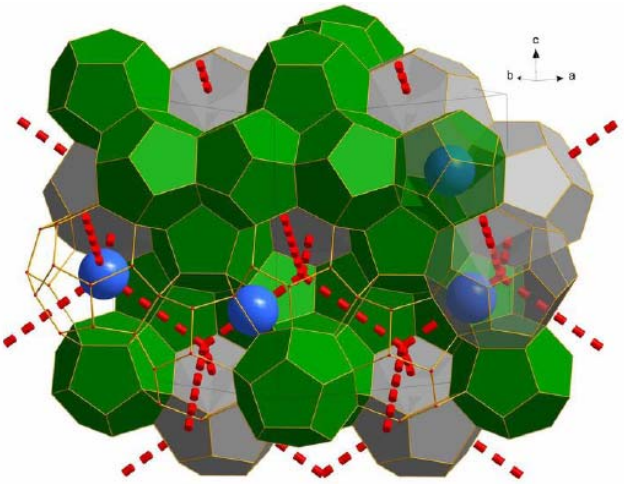

Fig.1. Leaching of Ne atoms (in blue) from the sII clathrate structure. Gas molecules can easily travel between large cages (in gray) passing through six-membered rings of water molecules (red dashed lines). Removal of Ne atoms from the small cages (in green) requires the presence of a water vacancy in one of the five-membered rings.

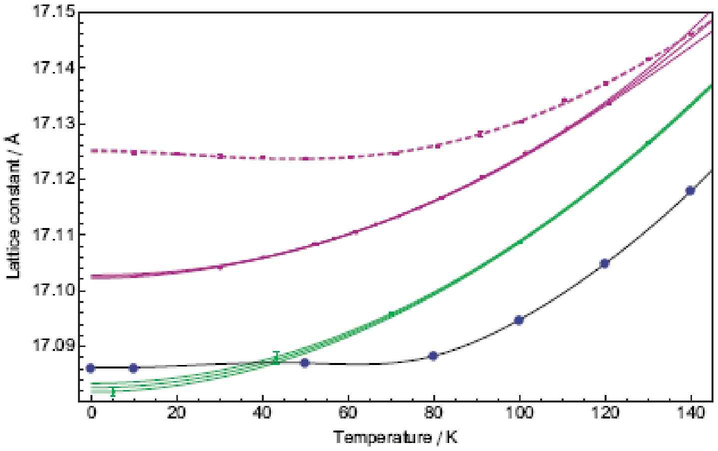

Fig.2. Lattice constants *a* versus temperature *T* and polynomial fits of the empty (magenta dashed), Ne- (magenta solid) and N_2-filled (green) sII clathrate hydrates together with confidence bands (±1σ). The blue points, together with a cubic spline interpolation as guide to the eye, correspond to the predicted values from lattice dynamical MD work.

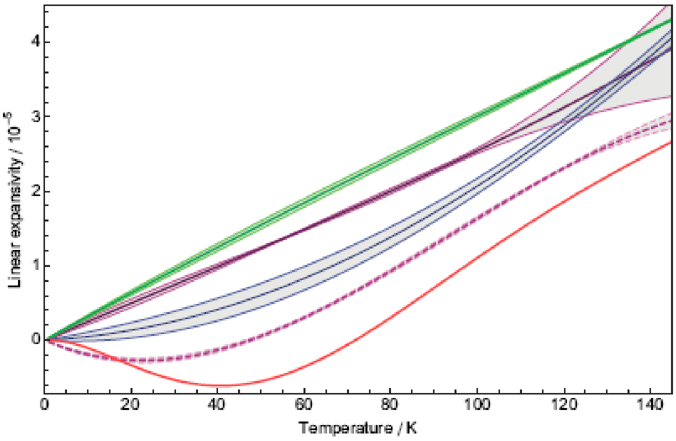

Fig.3. Linear expansivity $(\partial a/\partial T)/a$ versus temperature *T* of the empty (magenta, dashed), Ne- (magenta, solid) and N_2-filled (green) sII clathrate hydrates together with confidence bands (±1σ) as resulting from the polynomial fits of the lattice constants. The red curve describes the isotropic linear expansivity of deuterated ice Ih. The black curve together with confidence bands (±1σ) correspond to a polynomial fit to the predicted values from lattice dynamical MD work.