Experimental report

07/09/2015

Proposal:	**5-25-226**	**Council:**	4/2014

Title: The empty clathrate hydrate sII structure and its refilling with helium

Research area: Other...

This proposal is a continuation of 5-25-217

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Samples: 136D2O * 0-32 (Ne or He)

Instrument	Requested days	Allocated days	From	To
D20	4	4	04/09/2014	08/09/2014

Abstract:

The empty clathrate hydrate structure is the reference frame for predictions of gas hydrate properties and is of eminent importance as a reference point for our understanding of gas-water interactions in these guest-host compounds. In a previous experiment (5-25-217) we have attempted to form this empty hydrate structure by pumping out neon atoms of a neon-clathrate. We came quite close but due to scheduling constraints could not fully accomplish this task. We now propose to complete the emptying process and in this way form the lowest density form of condensed water known so far. Moreover, we would like to re-fill the empty hydrate structure with helium atoms to form for the first time a helium clathrate hydrate. Its structure and themal expansivity will be studied and compared to the empty hydrate as well as the structurally identical Ne-, Ar-, and Kr-clathrates. This will allow us to quantify the van der Waals interactions between water and the various noble gases in terms of the resulting volume changes. This then will provide valuable benchmarks for recent ab-initio attempts to better understand guest-host interactions in clathrates.

The empty clathrate hydrate sII structure and its refilling with helium (5-25-226)

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Gas hydrates form a large family of inclusion compounds in which gas molecules or atoms are encaged into a crystalline framework of H-bonded water molecules. Guest molecules stabilise the open water-host framework. Removing the guest atoms destabilises the host lattice and, consequently, the empty hydrate lattice was considered experimentally inaccessible. This empty hydrate was and, in a modified form, it still is the basis of more than 30 years of thermodynamic predictions of gas hydrate stabilities and composition, for chemical engineers e.g. in problems related to flow assurance of gas and oil pipelines as well as in geo-engineering. Likewise, the empty clathrate is the reference frame for numerous quantum chemical calculations or molecular dynamics simulations [1-4], aiming at quantifying gas-water interactions in these guest-host systems. Two main structure types of gas hydrates are known, sI and sII clathrate hydrate, both of cubic symmetry. The empty sII-hydrate structure has been predicted to be the stable form of water below 275K at negative pressures [5,6]. In 2013 we have produced, for the first time, empty hydrate of structure sII and determined its crystal structure, thermal expansivity and stability limit. This work was published in Nature last year [7]. We had 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. In contrast to the filled hydrates, and similar to ice Ih, the empty hydrate structure exhibits negative thermal expansion below ~ 55 K, 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.

Based on these results we had proposed to further study the influence of other guest molecules on the water framework. The simplest conceivable guest molecules are noble gases; their spherical shape and the pure van der Waals nature of interaction with the water cages make them ideal substances to study water – gas interactions in the crystalline state which is of fundamental importance in understanding and predicting gas hydrate properties. The simplest molecule of those is helium. Yet, while a clathrate hydrate of helium may possibly exist [8], its direct preparation form ice Ih turned out to be very challenging and thus it has never been unequivocally experimentally established. We wanted to use the unique chance to form this hydrate by refilling the empty hydrate and produce this highly interesting compound permitting a detailed comparison of structure and T-dependent lattice constants (expansivity). In this way we want to **quantify the van der Waals interactions between water and the various noble gases in terms of the resulting volume changes** (as compared to the empty hydrate). To complete this series we also planed to measure structure and expansivity of sII Ar- and Kr-clathrate (prepared in Göttingen).

D20 was ideally suited for the proposed experiment with its *in-situ* capabilities for following the He-filling, its flexibility for switching between the kinetic and lattice expansivity work (high flux) and the detailed structural work of the formed clathrates (high resolution, short λ).
Using our well-established procedure [7] we have prepared pure Ne-hydrate samples in Göttingen with fully characterized particle size for the off-beam pumping in an orange cryostat at ILL prior to the allocated beam-time. We have completely redesigned, manufactured and tested a sample stick for this pumping exercise which allows to mount a standard ILL V-can, compared to the earlier experiments it has a Cernox-

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sensor and is otherwise very similar to the standard D20 sample stick; in this way we could avoid the transfer of the sample for the expansivity run (which was necessary in earlier experiments as only a Pt-sensor was mounted on our old pumping stick making low-T readings unreliable). The pumped sample was structurally studied on D20 (at 5K) and expansivity data were taken up to 140K (i.e. somewhat below the stability limit). The empty hydrate sample was then exposed to helium atmosphere at ~130K at 1 bar and the initial gas uptake as well as possible changes in lattice constants be studied *in-situ*. As the He filling was very low we have boosted the filling by using the ILL He-compressor (this needed a sample recovery at liq.N_2 and re-insertion into a gas pressure cell). In the following expansivity run we have observed very little change of lattice constants up to 70K (in contrast to the empty hydrate which shows negative thermal expansion [7]). Between 70 and 80K the sample started loosing He with a concomitant (isothermal) increase of lattice constants (as expected from our earlier work on Ne [7]).

As planned we have also measured the low temperature structure of sII Ar- and Kr-clathrate as well as their expansivities up to 140K. We have added a similar study on D_2-clathrate (originally not foreseen as we had no sample at hand during the writing of the proposal) which was prepared at HMI/ Berlin with the help of Dirk Wallacher.

In addition to the experimental program spelled out in the proposal we have attempted to produce the empty sI structure by starting from a sI N_2-clathrate prepared in Göttingen. Usually N_2-clathrate crystallizes in the sII structure (see e.g. [7]) but we had established a recipe [9] to produce a clean sI N_2-clathrate. The attempt to pump on this structure at 142 K was, however, not very successful. The emptying was very slow and there was little hope to proceed in this way to produce the empty sI structure.

Finally, we like to mention that the first part of the experiment was done at a nominal reactor power of 35 MW (due to a cold source problem) with a premature shutdown on 07/09/2014. Some time was recovered after the startup on 10/09/2014 (before and into our next scheduled beam-time 5-25-225 starting officially on 12/09/2014).

References:

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