Experimental report

29/09/2017

Proposal: **5-25-254** **Council:** 4/2016

Title: Guest-host interactions and lattice expansivities in clathrate hydrates

Research area: Physics

This proposal is a new proposal

Main proposer: **Werner Friedrich KUHS**

Experimental team: Thomas HANSEN
Werner Friedrich KUHS

Local contacts: Thomas HANSEN
Michael Marek KOZA

Samples: O2, N2, Xe, CO2 *6D2O

Instrument	Requested days	Allocated days	From	To
D20	3	3	31/05/2016	01/06/2016
			20/09/2016	22/09/2016
IN6	6	6	30/05/2016	01/06/2016
			21/09/2016	26/09/2016
IN4	4	4	01/09/2016	05/09/2016

Abstract:

The interactions of guest molecules/atoms with the water frame in clathrate hydrates (gas hydrates) were recently found to be considerably stronger than previosuly assumed. This has important consequences for the understanding of water interactions in general and it helps to explain the observed lattice constants and expansivities of gas hydrates. Moreover, very different behaviour of the guest rattling modes were observed ranging from highly harmonic (Xe) to highly anharmonic (N2). At this stage we are unable to quantify the link between rattling modes, their anharmonicity and the lattice expansivity. Yet, in recent work we could show that the description of guest modes with an Einstein oscillator model can capture some of the anomalous features of lattice expansivity. Now we want to study this link for some exemplaric systems (N2, O2, CO2- and Xe-clathrates) by combining diffraction (expansivity) and inelastic scattering work (rattling modes). These clathrates differ significantly in their guest mode anharmonicity and lattice expansivities and should thus allow to test the range of applicability of the dynamic models constructed.

Formation kinetics of Ne-clathrate (5-25-225)

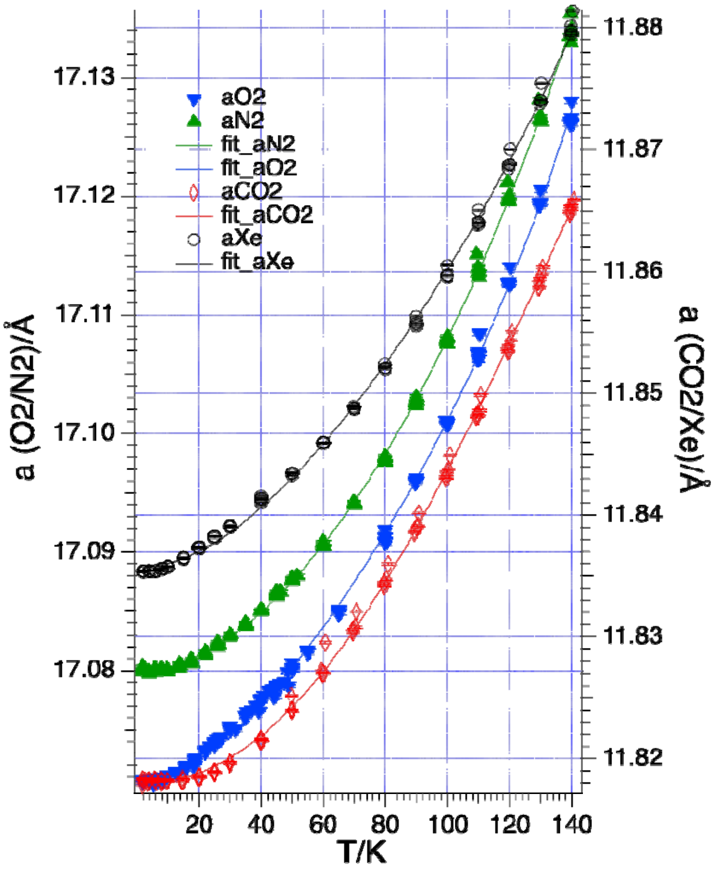
Thomas C. Hansen[a], Michael M. Koza[a], Oliver Zimmer[a], Andrzej Falenty[b] and Werner F. Kuhs[b]
[b] Institut Laue-Langevin (ILL), 6 rue Jules Horowitz, BP 156, 38042 Grenoble Cedex, France
[a] GZG Abt. Kristallographie, Universität Göttingen, Goldschmidtstr. 1, 37077 Göttingen, Germany

Gas hydrates (clathrates 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 [1]. Understanding the interactions between guest atoms or molecules and the water host structures is of crucial interest for prediction of phase stability and hydrate composition in geology and chemical engineering, in particular for the economically very important area of flow assurance in gas and oil-pipelines [1,2]. We have recently managed to form the empty clathrate structure of type II, which gives us a direct means of comparing empty and filled gas hydrates; this gives us important insight into the gas-water interactions in clathrates [3]. It turns out that the presence of guest molecules not only stabilizes the empty gas hydrates structures by acting as a spacer but also leads to considerable lattice shrinkage indicating fairly strong attractive interactions between water and small guest molecules like N_2, Ne or H_2. The T-dependent lattice constants of further gas hydrates were published recently [4] demonstrating that guest-host interactions are much stronger than previously assumed for gas hydrate prediction. Moreover, the data suggested a very particular low-temperature behaviour which could be rationalized by an early onset of guest rattling modes which – at least for CO_2 and Xe – could well be cast into a harmonic Einstein oscillator model [4]. It emerges that accurate T-dependent lattice constant measurements could give deep and quantitative insights into guest-host interactions and allow in principle to distinguish between different concurring descriptions ranging from a pure Einstein over mixed Einstein-Debye to lattice dynamical Debye-models; they differ in particular in the low-temperature region – a region which was only superficially investigated in our earlier work [4]. The purpose of our proposal was (1) to get a distinctly denser mesh of temperature data points at temperatures below 140K, and (2) to study the mode frequencies of the guest atoms by inelastic neutron scattering on IN4 and IN6 to link the Einstein fit parameters for the lattice constant to these eigen-frequencies.

D20: Samples of Xe-, CO_2-, N_2- und O_2-clathrate (the latter in the context of proposal 1-10-33) were studied on D20 at a wavelength of 1.54393Å (monochromator take-off 90°) with steps of 2K below 10K (lowest T 1.9K), 5K below 50K and 10K up to 140K. The data were of sufficient quality not only to refine the lattice constants but also the structural parameters of host-structure and guest atoms or molecules. As the lattice constants were sensitive to the varying sample position inside the cryostat, the absolute values were pin-pointed to synchrotron results on the identical samples in the same way as described in [4]; the resulting T-dependent lattice constants are plotted in Fig.1. Clearly, at low temperatures CO_2-clathrate has the lowest values normalized by the number of water molecules in the unit cell, indicative of the strongest water-guest interactions for the four guest species investigated. The attractive O_2-water interactions are clearly stronger than for N_2 which is probably due to the stronger quadrupole moment of oxygen.

We also note that the low-temperature refinements show an intriguing increase of atomic displacement parameters for the guest atoms (most pronounced for O_2 and N_2 in the large cages but also visible for O_2 in the small cages; although a final interpretation cannot be given at this stage, a peculiar behavior below 20K is also seen in some of the inelastic data. Clearly, these effects could be seen only by using the finer steps in temperature, which was the purpose of the proposal.

IN4 and IN6: Samples of Xe, CO_2- and N_2-clathrate were investigated on IN4 at a wavelength of 3.0Å at 1.5K as well as 10, 20, (30), 40, 60, 80, and 100 K; the Xe-hydrate sample was also measured at 2.2Å at 1.5, 10, 20, 40, 60, 80, and 100K. On IN6 the same samples were measured at a wavelength of 5.12Å at temperatures of 1.5K as well as 10, 20, 40, 60, 80, and 100 K. The data confirm the strong anharmonic behavior observed for the rattling of N_2 in the large cages and the much smaller anharmonicity for Xe-hydrate [5,6] as shown in Fig.2. The lower characteristic frequencies of the guest atoms are likely to be linked to the large cage modes, which are well separated from the small cage modes in the case of Xe; these modes could be used as constraints in an Einstein model for the description of lattice expansivities [4].



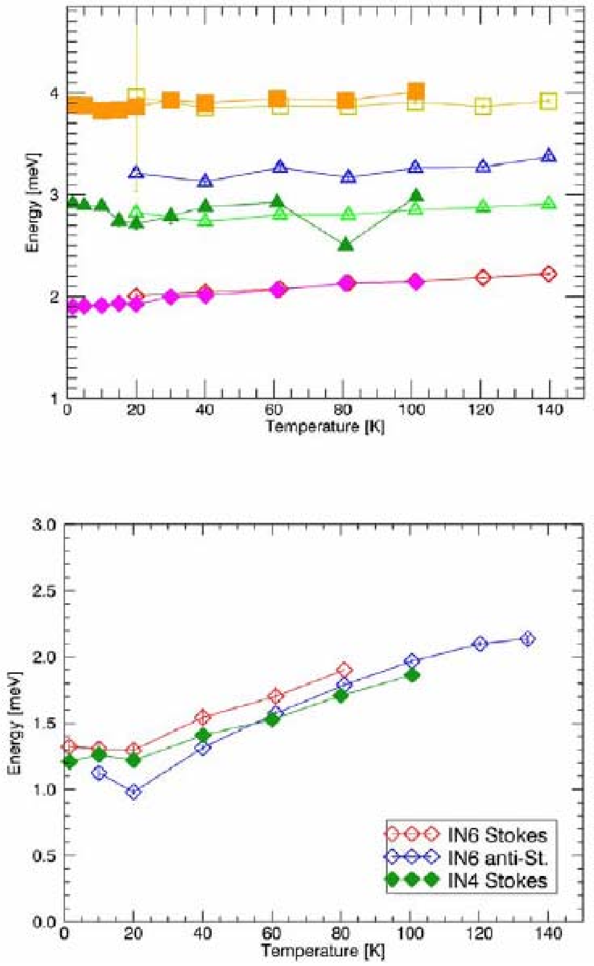


Fig.1 (l.h.s) Lattice constants of the various clathrates studied as a function of temperature. O_2-clathrate has distinctly smaller lattice constants compared to the isostructural N_2-clathrate. CO_2-clathrate has much smaller lattice constants and distinctly larger expansivity as the isostructural Xe-clathrate. The O_2-expansivity is remarkable constant between 20 and 50K for reasons not yet identified. **Fig.2.(l.h.s.) Top:** Temperature dependence of energies characteristic of localized Xe vibrations in Xe-hydrate compound. Full symbols correspond to mode energies identified at the Stokes line of IN4 data monitored with 3 Å. Open symbols correspond to data derived from the anti-Stokes line of IN6 signal monitored with 5.12 Å. The higher resolution data from IN6 allow to discriminate a weak intensity centred at about 3.2 meV (open blue triangles). Data are extracted from fits of a set of Gaussians to the density of states of Xe-hydrate**. Bottom:** Temperature dependence of N_2 characteristic frequency. Fits were carried out with a single Gaussian. Peak is outside the dynamic range above 80 K at IN6 Stokes line. At the anti-Stokes line the low-T data are affected by the duverging background (Bose statistics) below 40 K.

References: [1] ED Sloan & CA Koh, Clathrate Hydrates of Natural Gases, 2008, Boca Raton, CRC Press.
[2] CA Koh, ED Sloan, AK Sum & D Wu, Ann.Rev.Chem.Biomol.Eng. 2 (2011) 237-257.
[3] A Falenty, TC Hansen & WF Kuhs, Nature 516 (2014) 231-233.
[4] TC Hansen, A Falenty & WF Kuhs J.Chem.Phys. 144 (2016) 054301.
[5] B Chazallon, H Itoh, M Koza, WF Kuhs & H Schober, PCCP 4 (2002) 5809-4816.
[6] H Schober, H Itoh, A Klapproth, V Chihaia & WF Kuhs, Eur.Phys.J. E12 (2003) 41-49.