



Quasi-elastic neutron scattering investigation of the guest molecule dynamics in the bromomethane clathrate hydrate



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ABSTRACT

The bromomethane clathrate hydrate crystallizes into the type I structure with the six large cages and the two small cages both filled with bromomethane guest molecules. Dynamic properties of the guest molecules have been investigated by means of incoherent quasi-elastic neutron scattering (QENS) in temperatures between 50 K and 260 K at atmospheric pressure. These investigations provide direct experimental evidence about the fundamental aspect of rotational motions of the bromomethane molecules. A comprehensive study has been achieved through the analysis of the structure factors (i.e., the spatial extend of the motion) as well as of the QENS broadening (i.e., the characteristic time of the motion). Such analysis reveals the existence of two types of motions: methyl group rotations about the C–Br bond with activation energy of 0.19 ± 0.08 kJ/mol and whole molecule reorientations thermally activated above 100 K with activation energy of 4.3 ± 1.2 kJ/mol. At the lowest studied temperature (50 K), the methyl group rotates faster by almost one order of magnitude in the large cage (characteristic time of 1.25 ps) than in the small cage (characteristic time of 10 ps). Such results provide new experimental signatures of the cage occupancy by evidencing different Brownian dynamics for the guest molecules in small cages and those in large cages.

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1. Introduction

Among organic nanoporous materials, clathrate hydrates represent probably one of the most important one, in view of their broad impact in various areas such as energy, environment, flow assurance or gas engineering [1]. These systems are made of guest molecules embedded within polyhedral cage-like structure (host lattice) formed by means of water molecules. Polygonal rings of water molecules connected at their edges by means of hydrogen bond insure the cage stability. These cages may adopt numerous arrangements to form a three-dimensional crystalline structure, depending on the chemical nature of the encapsulated molecules. Under appropriated thermodynamic conditions, clathrate hydrates crystallize into two major types of structures: the cubic structures

termed type I and type II [2,3]. More specifically, the type I structure corresponds to a 12 Å cubic unit cell composed of two small 5^{12} cages (the 5^{12} nomenclature refers to a cage formed with 12 pentagonal water rings) and of six large $5^{12}6^2$ cages [1].

Analyzing the dynamics of the guest molecules encapsulated within water cages leads to explore the potential energy surface as seen from the guest molecule inside the cage [4]. In the case of systems rich in hydrogen like clathrate hydrates (the hydrogen atom possess the largest known incoherent scattering cross section), incoherent quasielastic neutron spectroscopy [5] is particularly appropriated for such an investigation, as it has been shown for hydrogen clathrate hydrates [6] or super-protonic conducting clathrate hydrates [7–9]. In the case of methane clathrate hydrate, numerous works have been devoted to the guest molecules dynamics, exhibiting fundamentally interesting features. In this type I clathrate hydrate, almost free rotation and very anharmonic low-frequency translation (so-called rattling mode) are observed because of the large size of the cages [10–12]. The quantitative analysis of molecular dynamics at the lowest temperature leads to describe the molecular motion as single-particle quantum rotation

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† To our colleague who left us too soon.

in weak rotational potentials differing slightly from cage to cage [13]. This static distribution of the local environment owes to different arrangements of the hydrogen bonds in the cage surface.

While methane clathrate hydrate represents the prototypical non-polar system, very few studies deal with clathrate hydrate with polar guest molecules in the type I structure. The simplest such molecules are probably the methyl halides. The three light methyl halide hydrates ($\text{CH}_3\text{X}-5.75\text{H}_2\text{O}$ and $\text{X} = \text{F}, \text{Cl}$ or Br) assume the same type I cubic crystal structure as methane clathrate [14]. Larger guest molecules such as methyl iodide require larger cages and crystallize within the cubic II structure [14]. High energy resolution neutron scattering experiments have been performed to analyze the rotational tunneling of guest molecules in the series of methyl halide clathrate hydrates [15–19]. The methyl halide hydrates show quantum rotational dynamics of the CH_3 groups similar to the methane case. The analysis of their one-dimensional rotation requires simple mathematics, facilitating a more quantitative interpretation than the three-dimensional dynamics of methane molecules. These studies have revealed the existence of adsorption sites of the guest molecules at the cage surface. Combined molecular dynamics simulations and quasi-elastic neutron scattering analysis has confirmed such interpretation at higher temperature in the case the type II methyl-iodide clathrate hydrate [20]. In the case of methyl bromide clathrate hydrate, M. Prager et al. have used neutron spectroscopy in order to characterize the potential surface of the two different types of cages existing in the type I clathrate structure by analyzing the inelastic spectrum in the energy range from $50 \mu\text{eV}$ to 200 meV [18]. The tunneling spectrum obtained was interpreted as a superposition of four bands, three from adsorption sites in large $5^{12}6^2$ cages and one in small 5^{12} cages. The almost continuous distribution of barrier heights leads to “glasslike” quasielastic scattering, i.e. with very similar intensity profiles over temperatures up to ca. 100 K. The qualitative analysis of the elastic incoherent structure factor suggests that the methyl rotation gets mixed with the whole molecule tumbling in the cage above $T = 50 \text{ K}$. The aim of the present paper is to provide a comprehensive description of the dynamics of bromomethane molecules inside the clathrate by using quasi-elastic neutron scattering in temperature range up to 260 K. In this issue, the present analysis takes the advantage of analyzing the momentum transfer dependence of the quasi-elastic neutron scattering signal over a broad dynamical range to unravel geometrical and timescale information about the dynamical processes met in bromomethane clathrate hydrate.

2. Experimental details

2.1. Sample preparation

Samples with deuterated and hydrogenated host lattices were prepared while the guest molecules in this study are hydrogenated. The clathrate hydrate has been prepared by following the procedure described in Ref. [18]. Liquefied bromomethane was introduced into a reaction vessel containing frozen water with a stoichiometry 1:5.75 (to ensure the formation of the type I structure). The mixture was warmed up to about $20 \text{ }^\circ\text{C}$, leading to a pressure of about 6 bars. The liquid mixture was then slowly cooled down under permanent stirring. Once the solidification occurred, the reaction vessel was at atmospheric pressure, showing that all bromomethane has reacted to form the clathrate hydrate. The melting point of the type I bromomethane clathrate hydrate is $T_m \sim 9 \text{ }^\circ\text{C}$. All subsequent sample manipulations have been done under cold inert atmosphere.

2.2. Quasi-elastic neutron scattering experiments

The studied system was a clathrate of bromomethane in which the aqueous sub-structure was deuterated ($\text{CH}_3\text{Br}-5.75\text{D}_2\text{O}$), so that the scattering signal is mainly incoherent and originates from the bromomethane molecules. In this issue, only the dynamics of the encapsulated molecules will be analyzed. In order to check the deuteration of the sample, a fully hydrogenated sample has also been used. Neutron scattering experiments were performed with the cold time-of-flight (TOF) spectrometer NEAT at HZB (Berlin, Germany) with an energy resolution ΔE of about $100 \mu\text{eV}$ and with an incident wavelength $\lambda_0 = 5.1 \text{ \AA}$. Cold polycrystalline powder was filled into a flat Aluminum sample holder sealed with indium wire. The sample thickness was 1 mm for the deuterated sample and 0.4 mm for the hydrogenated sample. All sample manipulations have been performed under cold Nitrogen atmosphere (filling of the sample holder and cold-transfer into the cryostat of the spectrometer). The flat samples were oriented at 45° to the beam. To test whether the clathrate formation was successful, diffractograms were obtained at various sample temperatures between 5 and 260 K and QENS spectra have been recorded at temperatures ranging from 50 K to 260 K at atmospheric pressure. Empty cell spectra have been recorded for background correction and a vanadium spectrum has been used to correct for detector efficiency and to determine the experimental resolution function. The whole data reduction has been done by using the INX program [21,22]. In this procedure, the Bragg peaks have been carefully removed from the angular grouping for fitting the incoherent scattering law with the program NEMO [23].

2.3. Characterization of the bromo-methane clathrate hydrate

The integrity of the hydrate structure has been checked by indexing the Bragg peaks within the cubic I clathrate structure with a lattice parameter of 12.1 \AA and space group $Pm\bar{3}n$ [24], as shown in Fig. 1 at $T = 260 \text{ K}$. One can observe the existence of additional Bragg peaks originating from the hexagonal ice Ih [25,26]. The space group of the hexagonal ice crystal is $P6_3/mmc$ and its unit cell parameters $a = 4.518 \text{ \AA}$ and $c = 7.356 \text{ \AA}$ at 250 K [27]. Three peaks due to the presence of ice inside the sample container are observed and this ice contamination has been taken into account into the QENS data analysis, as described in the Supplementary Materials.

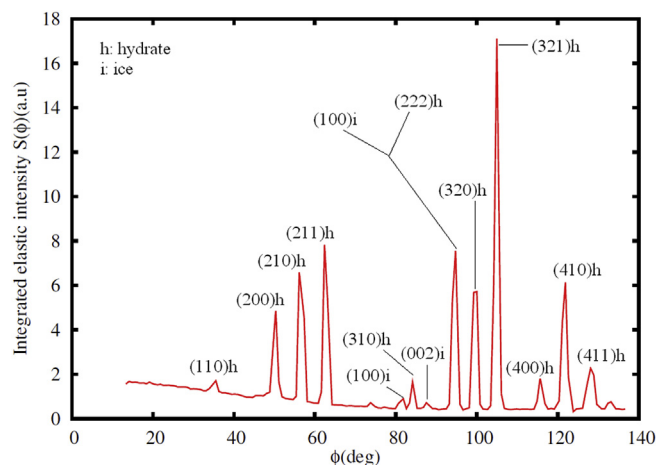


Fig. 1. Neutron diffraction pattern of the bromomethane clathrate hydrate at 260 K recorded with an incident wavelength of 5.1 \AA . Instrument: NEAT@HZB, Berlin. The Bragg peaks due to ice contamination are indicated with character *i* and those due to clathrate hydrate are indicated by character *h*.

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