THE STRUCTURE AND CAGE FILLING OF GAS HYDRATES AS ESTABLISHED BY SYNCHROTRON POWDER DIFFRACTION DATA

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ABSTRACT
Synchrotron powder diffraction data were measured on various gas hydrates prepared at different fugacities and recovered to low temperatures. The data extend to sin θ/λ values of at least 1.01 Å⁻¹, in some cases up to 1.48 Å⁻¹, i.e. at least 3 times further in reciprocal space than the best single crystal data obtained so far. Here the results of CO₂-hydrate are presented in detail. Structural information is obtained from Rietveld refinements to unprecedented precision. All H-bonded O-O distances are found to be close to 2.75-2.76 Å, i.e. very close to the values in ice Ih; differences between a hydrogenated and deuterated host lattice are insignificant. Cage occupancies were obtained for the first time in free refinements together with positional parameters of the guest molecule and their atomic displacement parameters. There is good agreement between the experimental cage occupancies and prediction results from CSMGem.

Keywords: crystal structure, cage filling, Langmuir model, synchrotron diffraction, powder diffraction, Rietveld analysis, CO₂-hydrate

INTRODUCTION
Gas hydrates are non-stoichiometric compounds of hydrogen-bonded water molecules organized in form of cages around guest molecules that stabilize the lattice [1]. The most common cubic structures sI and sII are composed of two types of cavities: large (LC) and small (SC). For a full understanding of the physical chemistry of these compounds the cage filling is one of the most important structural parameters. There is multiple evidence that the cages are not necessarily fully occupied, yet a precise determination of cage occupancies has proven to be quite difficult. Spectroscopic methods in general do not provide access to the absolute cage fillings and crystallographic methods are bound with problems due to the extensive disorder of both host lattice and guest position. Particularly severe are the parameter correlations between guest positional coordinates, guest position occupancy and the thermal displacement parameters of the guests. In order to disentangle these correlations usually one needs to fix some of these parameters which in turn will cast doubts on the remaining freely refined values. We will show further below that some of these correlations can be overcome by using very high quality synchrotron powder diffraction data extending to large scattering angles. In the following we shall look in particular at the often investigated case of CO₂ hydrate due to its complex disorder situation but will also mention briefly some other hydrates of importance.

The first structural study of (deuterated) CO₂ hydrates quoting cage occupancies was published in 1998 based on in situ neutron powder diffraction data [2]. While there was general agreement that the large cage should be almost completely filled, the small cage situation was unclear at that time. The structural model with its positional parameters and the displacement parameters had to be fixed in this preliminary

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