Microscopic Behavior of Gas Clathrates Studied by cold Time-of-Flight Neutron Spectroscopy

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Importance of nanostructured materials is growing from day to day. In general clathrate hydrates are inclusion compounds, formed by a network of hydrogen-bonded water molecules which are stabilized by the presence of foreign (generally hydrophobic) molecules. Methane clathrates, known for decades as « fire ice », are common constituents of the shallow marine geosphere. The clathrate hydrates with molecular hydrogen are another example of this kind of materials, which were synthesized just recently for the purpose of hydrogen storage. The guest molecules are hosted in cages of different forms and with typical dimensions of the cages range between 3 - 15 Å. There are indications that the size of the cages affects macroscopic properties important for the gas storage. For instance for clathrates where hydrogen molecules only occupy so-called small cages the loading pressure is reduced by almost one order of magnitude and the temperature stability increases by 100K compared to the clathrates where hydrogen occupies cages of larger dimensions. The origin of such behavior lies, however, in the microscopic interactions between the hydrogen and the host.
To understand the impact of the confinement on the behavior of guest molecules we have studied the dynamics of molecular hydrogen confined into cages of two different dimensions, 5.02 Å and 6.67 Å, by inelastic and quasielastic neutron spectroscopy complemented by molecular dynamics calculations. Neutron scattering spectroscopy is a powerful tool to study such systems since it delivers direct microscopic information in both space and time, while other spectroscopic probes are either local (such as hyperfine field methods) or macroscopic in the spatial dimension (such as light scattering). Time-of-Flight (TOF) spectroscopy with cold neutron allows us best to explore phenomena in condensed matter on the terahertz frequency range (10μeV -150meV) and on a length scale from 0.5 to 100 Å.
We have found that the mobility of the confined hydrogen strongly depends on the confinement dimensions. We observed large differences between the values of the mean square displacements in the large and small cages, giving evidence for the localization of the guest molecules in the small cage. Secondly, the localization leads to coupling between rotational and translation motions and to the onset of a new type of motion in the small cage. Both of these observations of quantum confinement deal with the stronger bonding between the hydrogen and the ice matrix in the small cage, which helps to improve the macroscopic properties.