**Inside the Clathrate Hydrate Cage**

Clathrate hydrates are solids that have a molecular structure in which gas molecules occupy so-called “cages” comprising hydrogen-bonded water molecules. When they are empty, the cages collapse into an ice crystal structure, but the presence of a gas molecule makes them stable. Clathrate hydrates have enormous practical importance as sources of energy, as hydrogen storage media, and as components of astrophysical bodies having methane molecules as the guest material inside their ice-like cage structures. Researchers using the XOR 3-ID beamline at the APS and the IN6 instrument at the neutron reactor source of the Institut Laue-Langevin have gained a better understanding of a particular clathrate hydrate that has wide implications for understanding the thermal properties of disordered solids, structural glasses, and other materials.

By using site-specific $^{83}$Kr nuclear resonant inelastic x-ray scattering (NRIXS) in combination with incoherent inelastic neutron scattering (IINS) and molecular-dynamics simulations, researchers from the University of Saskatchewan, the National Research Council of Canada, Argonne National Laboratory, the Universität Kiel, the Universität Dortmund, and Institut Laue-Langevin have pinpointed the reason for the anomalously low thermal conductivity of type-II Kr clathrate hydrate: extensive mixing of the localized anharmonic “rattling” motions of “guest” $^{83}$Kr atoms with host lattice phonons. Clathrate hydrates have enormous practical importance as sources of energy, as hydrogen storage media, and as components of astrophysical bodies having methane molecules as the guest material inside their ice-like cage structures. The explanation derived from this research has wide implications for understanding the thermal properties of disordered solids, structural glasses, and other materials containing localized oscillators. The NRIXS measurements were performed at the XOR 3-ID beamline of the APS, while the IINS measurements were performed on the IN6 instrument at the neutron reactor source of the Institut Laue-Langevin.

Samples of type-II Kr clathrate hydrate were prepared by continuously exposing a finely ground powder of H$_2$O ice to Kr gas in a reaction vessel for 7 days at a pressure of 30 bar and at temperatures in the -10 to 0°C range. Samples were recovered at 77 K and then shipped in liquid nitrogen to the Institut Laue-Langevin in Grenoble.

The IINS data demonstrated a very strong coupling between guest vibrations and those of the ice-like lattice and indicated that these interactions result in the anticrossing of phonon modes with the same symmetry. The NRIXS technique was used to characterize the dynamics of the guest atom alone, in order to permit an understanding of the separate contributions of the guest and host vibrations to the IINS data. Use of the $^{83}$Kr guest atom permitted this because it has a low-lying nuclear level at 9.4 keV that can be excited by synchrotron radiation (in other words, it is a Mössbauer nucleus). Nuclear resonance makes the NRIXS data sensitive only to the motions of the $^{83}$Kr guest atoms in the clathrate cages, with the cage vibrations themselves being rendered essentially invisible.

The site-specific NRIXS method showed unequivocally that the phonon coupling between the guest and the host leads to unexpectedly large anharmonic motion of the guest (Fig. 1). The large anharmonicity is the cause of the very low thermal conductivity of the clathrate hydrate and is a direct indication of the nature of the coupling between the host and guest vibra-
tions, as coupling through the anharmonic term of the interaction potential provides the means for scattering the lattice thermal phonons, leading to the marked reduction in the thermal conductivity of the clathrate.

Data were obtained at 35K, 50K, 70K, 85K, and 100K. The researchers found that the large anharmonicity persists even at very low temperatures. Although the thermal population of the rattling modes at temperatures below 38K is small, the presence of glass-like thermal conductivity at very low temperatures strongly suggests that the anharmonicity is intrinsic to the guest-host interactions. The researchers do not believe that the non-stoichiometry in the occupancy of the vacant sites is an important factor. They point out that, although the absolute thermal conductivity may change slightly with a small difference in guest concentration, such a difference does not affect the glass-like behavior of the thermal conductivity. — Vic Comello


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