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Inelastic Neutron Study of THF+D_2 Clathrates

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Gas hydrates (clathrates) are elevated-pressure (P) and low-temperature (T) solid phases in which gas molecule guests are physically incorporated into hydrogen-bonded, cage-like ice host frameworks. Storage of hydrogen in molecular form within a clathrate framework has been one of the suggested methods for storing hydrogen fuel safely, but pure hydrogen clathrates form at high pressures (~2 kbar), which makes them impractical as a solution for hydrogen storage. Recent work has demonstrated that it is possible to obtain up to 4 wt% hydrogen ice clathrates when tetrahydrofuran (THF) is used to promote the formation of the clathrates structure and hydrogen takes up double occupancy of the small cage and then also starts to fill the larger cages as the THF concentration is reduced. The other interesting feature of this phenomenon is that the pressure of hydrogen required to stabilize the clathrates at 280K is reduced by a factor of 60 to 5 MPa. Although the kinetics of formation and subsequent release of hydrogen is far from acceptable if these mixed clathrates were to be used as a hydrogen storage medium, it is possible that similar materials and engineering improvements could result in suitable materials relevant to the future hydrogen economy.

Neutron inelastic scattering (INS) has frequently been used to probe the quantum rotor transitions and vibrational density of states of hydrogen absorbed in a wide variety of substrates. Neutron INS measurements on hydrogen adsorbed in d-THF+D_2/D_2O ice clathrate were carried out on the Pharos spectrometer at LANSCE. In the absence of paramagnetic impurities the H_2 molecule converts slowly (tens of hours) from the J=1 to the J=0 quantum rotor state. At 10K, kT is approximately 1 meV and so neutron energy gain excitations above this energy arise from H_2 molecules still in the J=1 quantum rotor state.

Experiments at 8K yielded two excitations at neutron energy gains of approximately 14 and 4.7 meV as compared with the H_2 free rotor separation of 14.7 meV. These can only arise from two species of hydrogen adsorbed in the clathrate, under the influence of quite different crystal fields. There is also an excitation at a neutron energy loss of 9.3 meV, which must be a center of mass mode as it is not present in neutron energy gain. Further experiments and modeling are in progress to come to a detailed understanding of the adsorption sites of H_2 in THF/D_2O ice clathrate.