Intercage Diffusion of Hydrogen in a Z-type Metal Organic Framework

Y. Ji (UF Physics), J. Hamida (UF Physics), N. S. Sullivan (UF Physics)

Introduction

Studies of the thermodynamic properties of quantum gases in mesoporous structures at low temperatures are of great interest because: (i) unique quantum features determine the transport and dynamics when the de Broglie wavelength becomes comparable to the confining dimensions, (ii) zeolitic structures including the metal-organic frameworks are particularly promising for the storage and transport of hydrogen in a possible future hydrogen economy. NMR methods can provide a direct experimental measurement of molecular interactions and dynamics inside the cages of the MOF structure.

Experimental

Conventional pulsed NMR experiments were used to measure the nuclear spin-spin and spin lattice relaxation of hydrogen deuteride (HD) adsorbed in a Z-type metal organic framework Z-1200.[1] HD is studied rather than H_2 because of the conversion of ortho-H_2 to para-H_2 at low temperatures that complicates the analysis of the results. The adsorption isotherms are used to determine the filling factors and the experiments were dedicated to studying the relaxation rates for 1 molecule per cage of the Z-MOF.

Results and Discussion

For coverages of one molecule per zeolite cage the spin-spin relaxation time jumps abruptly at 17.5 K. The fit to the temperature dependence shown in **Figure 1** corresponds to a jump frequency $\tau_0^{-1}\exp(-E_{AC}/T)$ with τ_0^{-1} = 3.5 10^{10} s^{-1} and an activation energy E_{AC} = 72 K. These values are in close agreement with those reported for neutron scattering studies for HD in AlPO4. [2]

Conclusions

Measurements of the nuclear spin-spin relaxation times of HD at low filling factors in a Z-MOF show a high rate of diffusion consistent with neutron scattering experiments.

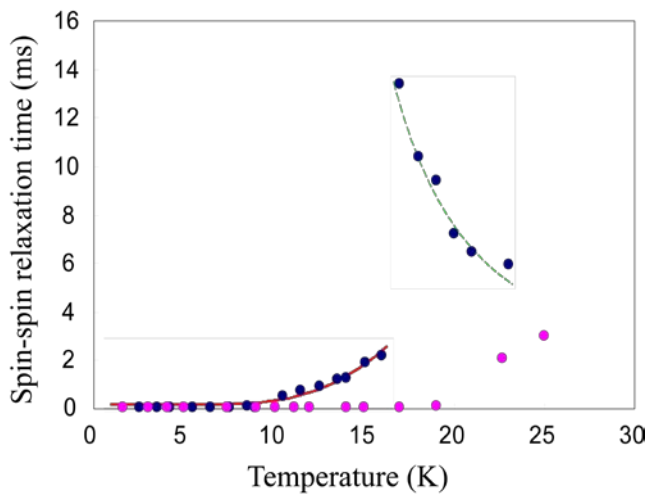

Figure 1. Observed temperature dependence of the nuclear spin-spin relaxation of HD in Z-MOF. Solid blue circles for 1 molecule per cage, purple circles for 0.1 molecules per cage.

References

[1] Sigma Aldrich, St. Louis, MO 63103, Basolite (®) , Z1200.
[2] Coulomb, J.P., Floquet, N, Dufau N, Llewellyn, P, and Andre G, Micro & Mesoporous Materials, **101**, 271 (2007).