NMR Studies of Methane Adsorbed in the Interior Cages of Zeolite 13-X

Yu Ji (UF-Physics), J.A. Hamida (UF- Physics), N.S. Sullivan (UF-NHMFL)

Introduction

The high symmetry cages of the alumino-silicates known as *zeolites* are of considerable current interest because of their potential for storing combustible gases such as hydrogen and methane. While these materials show high molecular adsorption capacities, little is known about the molecular state of the adsorbed molecules. Are the molecules orientationally ordered or disordered? Do they form hindered rotor states, or do they undergo rotational diffusion at low temperatures? These features are important as they provide information about the interaction between the molecules and the adsorbant and the kinetics of desorption. These latter parameters are the critical ones for evaluating materials for hydrogen and methane storage in any consideration of a realistic hydrogen economy.[1]

Experimental

Pulsed NMR techniques were used to measure the nuclear spin-spin relaxation time and the nuclear spin-lattice relaxation time for a monolayer of methane adsorbed on crushed *zeolite* type 13X [2]. Measurements of the adsorption volume as a function of temperature were used to estimate the monolayer coverage. The NMR measurements were carried out at a low Larmor frequency in order to have manageable spin-lattice relaxation times at low temperatures. The nuclear spin-spin and spin lattice relaxation times were measured using both 90_x - 90_x and 90_x - 90_y radio-frequency pulse sequences to measure the liquid-like and solid-like echoes, respectively.

Results and Discussion

The temperature dependence of the nuclear spin-lattice relaxations is shown in Fig. 1. Different symbols refer to different samples condensed onto the *zeolite.* The most remarkable feature is the onset of a strong temperature dependence at about 15 K. This dependence is interpreted as arising from the energy separation between the A and T species of methane molecules in orientationally ordered monolayers of methane adsorbed on the interior surfaces of the *zeolite* cages.

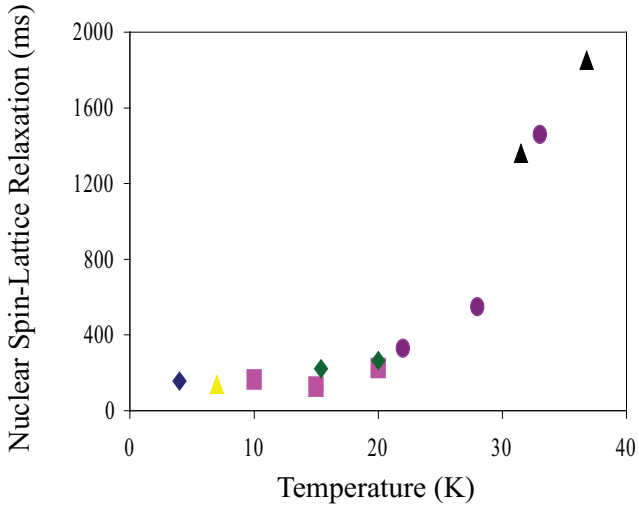

Fig. 1. Temperature dependence of the nuclear spin-lattice relaxation time for a monolayer of methane on zeolite-13X.

Conclusions

Measurements of the spin-spin and spin lattice relaxation times for methane adsorbed in *zeolite* suggest that the molecules have fixed centers of mass but thermal excitations from the ground state (A symmetry) to the next highest level (T-symmetry) state apparently determine the relaxation times.

References

[1] *Basic research needs for the hydrogen economy*, U.S. Department of Energy**,** Office of Science, May, 2003. Report of Basic Energy Sciences Workshop.

[2] Linde molecular sieves type 13X, lot No. GL-945383-2, Union Carbide Corporation, P.O. Box 372, South Plainfield, N.J. 07080.