Nuclear Spin Relaxation Spectroscopy for Determining Molecular Kinetics

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Introduction
Application of a novel technique of nuclear relaxation spectroscopy is reported for measuring the critical molecular kinetics of light molecules trapped in mesoporous structures. The measurements are particularly valuable for assessing adsorption materials that have potential for use in hydrogen or methane storage systems [1], or for carbon dioxide sequestration [2]. The method is, however, quite general and can be used when the relaxation process is determined by weak thermal couplings between different energy reservoirs. This is illustrated in Fig.1 showing the overall relaxation path for two weakly coupled energy baths, one of which is virtually isolated from the lattice. The overall relaxation rate is given by \( R_{\text{Tot}} = \frac{(C_{T_a} + C_{T_b} + C_A)/C_A) R_{\text{AB}}}{C_A} \) where \( R_{\text{AB}} \) represents the weak interbath coupling rate.

Experimental
As an example of the use of this technique we have carried out pulsed nuclear magnetic resonance studies of methane trapped in zeolite-13x. The goal of the experiments was to determine (i) the spectrum of rotational excitations of the molecules in the zeolite cages, and (ii) the thermal activation energy for diffusion through the zeolite structure. Measurements of the methane adsorption isotherms were first carried out to determine the exact filling of the cages for one molecule per sodalite cage. This value was marked by a sharp step in the adsorption isotherm [3].

Results and Discussion
Methane has three different molecular species: para, ortho, and meta with total nuclear spin \( I=0,1 \) and 2, respectively, corresponding to the three distinct ways of satisfying the Pauli principle for the exchange of protons in the molecular structure. These are also described by the E, T and A symmetry states of a tetrahedral rotator. Only the A and T symmetry states can be studied by NMR. The relaxation path is studied by applying an RF pulse to perturb (heat up) the nuclear spins and the recovery is determined by monitoring the NMR echo amplitudes. The nuclear spin lattice relaxation was measured for \( 4<T<100 \) K. Two sharp peaks were observed at \( T = 27 \) and \( T = 48 \) K [3]. These peaks are close to the values of the rotational energy level separations observed for methane adsorbed on graphite [4] and in these studies are attributed to the two T symmetry states for the symmetry sites in the sodalite cage.

Conclusions
Nuclear relaxation spectroscopy has been used successfully to determine the separation of the energy levels of the A and T symmetry states of methane trapped in zeolite.

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References