NMR Study of HD Adsorbed in a Z-type Metal-Organic Framework

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Abstract.
We report the results of measurements of the nuclear spin-lattice and spin-spin relaxation rates of hydrogen deuteride trapped in the mesoporous cages of a metal organic framework (MOF) for temperatures $2.2 < T < 50$ K. There is considerable interest in the use of this class of materials for hydrogen storage because of the high density of adsorption. NMR studies can provide important information about the molecular interactions and dynamics inside the cages of the MOF structure. Samples were studied with filling factors of 0.1 and 1.0 molecules per cage as determined by the adsorption isotherm at 77 K. The results show strong peaks in the relaxation times at several well defined temperatures that are very different from the adsorption energy levels. The origin of these peaks is discussed in terms of the quantization of the translational degrees of freedom of the molecules inside the cages and the associated discrete energy levels. Measurements of the nuclear spin-spin relaxation times also provide an important measure of the diffusivity of hydrogen through the MOF structure which is a critical parameter for the use of MOFs for storage and transport.

1. Introduction
Studies of the thermodynamic properties of quantum gases ($\text{H}_2$, $\text{HD}$, $\text{^3He}$, $\text{^4He}$) in mesoporous structures at low temperatures are of great interest because (i) unique quantum features determine the transport and dynamics when the DeBroglie wavelength becomes comparable to the confining dimensions, and (ii) zeolitic structures including the metal-organic frameworks[1, 2, 3] are particularly promising for the storage and transport of hydrogen in a future hydrogen economy[4, 5]. The dynamics and interactions of the molecules in these structures can be explored by measuring the NMR relaxation times. The dipolar interactions of the molecules are modulated by the motion of the molecules and the NMR relaxation times therefore depend on the thermal excitations of the molecular energy levels and their coupling to the surroundings. We studied the behavior of HD rather than $\text{H}_2$ in the confined geometries to avoid uncertainties that would result from the conversion of ortho-$\text{H}_2$ to para-$\text{H}_2$[6] in zeolites and metal organic frameworks.

2. Experimental Methods
The Z-type metal-organic framework Z-1200 [7] was used for these studies because of its simple zeolitic structure with large supercages of octagonal section and small tetragonal openings of the order of 5-6 Å. This structure is an approximate but practical realization of a cage structure with almost spherical cavities of the order of 13 Å for the trapped hydrogen. The filling of the
framework was determined by measuring the adsorption isotherm at 77 K. The variation of the equilibrium pressure as a function of the number of molecules admitted shows a distinctive step (Fig. 1) as a filling of 1 molecule per cage is reached.[8]

![Figure 1. Adsorption isotherm of CH₄ on Z-MOF at 77 K. The step at 7 units correspond to a filling of one molecule per supercage. The total volume of gas adsorbed at this filling is in agreement with the known surface area of the material.](image)

The MOF was activated by heating to 350° C in vacuum for five hours. The powder was then lightly packed around a brush of copper wires that provided thermal contact to the walls of a sealed sample cell. HD gas was admitted via a heated capillary and the cell was maintained at a constant temperature using a feed back current that was proportional to the difference of the readout of a calibrated carbon glass thermometer and a set point. A small amount of ⁴He exchange gas provided a weak thermal link to an external liquid helium bath enabling studies to be carried out from 1.6 to 40 K.[9]

Pulsed nuclear resonance techniques were used to measure the relaxation times. Nuclear spin echoes were observed for 90°-τ-90° RF excitations, and the spin-spin relaxation times were determined from the decay of the echoes as a function of τ. The spin-lattice relaxation times were measured by observing the echo decay as a function of the repetition rate of the pulse sequences for a fixed τ. A fast recovery duplexer with active feedback was used to record the NMR signals.[10]

3. Results

The observed temperature dependence of the nuclear spin-lattice relaxation times for the temperature range 1.6 < T < 25 K is shown in Fig. 1. The limit of 1.6 K was the lowest temperature attainable by pumping the liquid helium bath. Four peaks are clearly visible at temperatures of 4.6, 6.3, 7.2 and 12.4 K, with a possible fourth near 1.5 K. These peaks are attributed to the discrete energy levels for the translational motion of the HD molecules in the quasi-spherical cage of the MOF. For an effective diameter d, the energy levels are given by $E_{n,l} = (\hbar k_{n,l})^2/2md^2$ where $k_{n,l}$ are the n-th roots of the l-th order spherical Bessel function. [11] These energy values are listed in table 1 for $d = 13$ Å, the largest sphere that can be inscribed in the Z-MOF supercage.

The observed relaxation following an RF pulse depends on the coupling of the nuclear spin degrees of freedom to other degrees of freedom (translational motion) and ultimately to the phonons of the MOF structure. After an RF pulse the nuclear spins reach a common spin temperature very rapidly on a time scale $\sim M_2^{-1/2} \sim 10^{-3}$s. where $M_2$ is the rigid lattice NMR second moment.

The coupling of the translational motion of the molecules to the phonon bath is, however, much slower because of the acoustic mismatch [12] between the phonons of the MOF and the translational excitations. From this mismatch we estimate an intrinsic bottleneck relaxation time $\tau_{int} \approx 10 – 50$ s. In this case the observed relaxation is determined by the heat capacities
Table 1. Energy eigenvalues $E_{n,l} HD$ in a well of width $d = 13\text{Å}$. $n$ designates the $n$th root of the Bessel function $j_l(kr)$.

| $l$ | 1   | 2   | 3   | 4   | 5   |
|-----|-----|-----|-----|-----|-----|
| $n = 1$ | 0   | 1.96 | 4.41 | 7.41 | 10.8 |
| $n = 2$ | 5.62 | 9.48 | 13.9 | 10.9 |
| $n = 3$ | 14.99 |  |  |  |

of the different thermal baths in the relaxation process, and the observed relaxation has been shown by Guyer, Richardson and Zane [13] to be given by

$$T_{1\text{(obs)}} = (1 + \frac{C_T}{C_P})\tau_{int}$$

(1)

where $C_T$ and $C_P$ are, respectively, the heat capacities of the translational excitations $E_{k,j}$ of the HD molecules and the phonons of the thermal bath. We would expect that $C_T$ would be given by a sum of Schottky heat capacities [14] but as seen in Fig. 2 the temperature dependencies are much sharper. To obtain a more realistic fit we used a Gaussian contribution for each $E_{n,l}$ as calculated by Stroud et al.[15] for a cell model of CH$_4$ in zeolite. The corresponding fit is shown by the broken line in Fig. 2. We have also measured the relaxation times for a coverage of $x = 0.1$. There is more scatter in the results but the peaks in $T_1$ are observed at the same temperatures.

![Figure 2](image1.png)

**Figure 2.** Temperature dependence of the nuclear spin-lattice relaxation time for HD in Z-MOF. for a coverage 1.0 molecule per cage. The broken line is the calculated dependence described in the text.

![Figure 3](image2.png)

**Figure 3.** Temperature dependence of the nuclear spin-spin relaxation time for HD in Z-MOF. Purple, $x = 0.1$, blue, $x = 1.0$ molecules per cage. The jump at $T = 17$ K marks the onset of intercage diffusion.

In Fig. 3 we show the temperature dependence of the nuclear spin-spin relaxation times. An abrupt transition is observed at $T = 17$ K which is attributed to the onset of intercage diffusion. The thermal activation represented by the solid red line below 17 K corresponds to a jump frequency $\tau_0^{-1}\exp(-E_{AC}/T)$ with $\tau_0^{-1} = 3.5 \pm 2.0 \cdot 10^{10}$s$^{-1}$ and $E_{AC} = 72 \pm 3$ K. These values are in good agreement with those reported by neutron scattering studies for HD in AlPO$_4$ and MCM-41.[16, 17]
The temperature dependence of $T_2$ for $T > 17$ K follows that expected for a dilute gas for which $T_2 \propto \eta/T$ where the viscosity $\eta \propto T^{1/2}$.[18]

4. Conclusion
Measurement of the nuclear spin-lattice relaxation of HD in the mesoporous cages of a Z-MOF show a strong temperature dependence with peaks in the value of $T_1$ at temperatures very close to those estimated for the quantized translational energy levels of an HD molecule constrained to the supercages of the MOF. In addition, the values of the spin-spin relaxation times show a high mobility for the HD molecules, consistent with neutron scattering studies.

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