

Transport through unidimensional nanochannels: the potential of pulsed field gradient and hyperpolarized tracer exchange NMR spectroscopy

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1. Introduction

The physical properties of confined molecular species diffusing inside the channels with comparable diameters has attracted a lot of attention over the last few decades due to their high relevance for a number of potential industrial applications, such as separations and catalysis. At the same time, diffusion processes in reduced dimensionalities reveal many interesting phenomena, including “single-file” type of diffusion [1]. In the present contribution we demonstrate the potential of the hyperpolarized two-dimensional tracer exchange and pulsed field gradient (PFG) NMR techniques to probe diffusion processes of pure single component and binary sorbate mixtures in the case of normal diffusion and under conditions of induced single-file diffusion inside nanochannels.

2. Experimental part

Since the character of molecular propagation is highly dependent on the quality of synthesized adsorbents, the use of sufficiently ideal (free of defects) nanostructures becomes of crucial importance for this type of studies. Recent progress in fabrication and modification of single-walled nanotubes (SWNT) with monodisperse inner diameters [2] has allowed the synthesis of novel aluminosilicate structures with sufficiently high channel length (~1000 nm) and diameter (~1 nm). Another nanoporous material, having 0.8 nm inner diameter and reported distribution of lengths of the crystals ranging from 500-600 μm - crystals of molecular wheels [3], has also been utilized. The necessity of sufficient tube length is sometimes prescribed when it is needed to minimize the contribution of the molecular exchange between different nanotubes to the measured diffusivity.

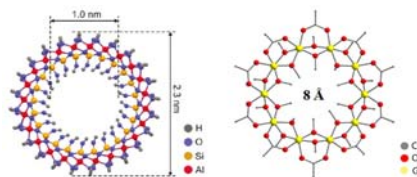


Fig. 1: Structures and dimensions of the aluminosilicate SWNT (left) and Ga10-wheel (right).

PFG NMR is a well-established technique for measuring self-diffusivities of adsorbed molecules. In the present study, a spectrometer with high (up to 30 T/m) gradient strength and high magnetic (17.6 T) field has been used to measure the effective diffusivity of various ^{13}C -labelled sorbates in the nanochannel system using ^{13}C PFG NMR. In comparison to ^1H PFG NMR, a key advantage of ^{13}C PFG NMR for studies of confined diffusion in nanotube samples is related to significantly higher effective T_2 NMR relaxation times. The diffusion decay stacked plot of spectra taken on $^{13}\text{CF}_4$ in aluminosilicate SWNT at 2 ms diffusion time is shown in Fig. 2.

The concept of the tracer exchange NMR method utilizing hyperpolarized ^{129}Xe atoms is illustrated in Fig.3. Exchange between the intracrystalline and gaseous phases under conditions of sorption equilibrium can be studied by following the change in the measured amplitudes of the chemically shifted signals of Xe atoms. In addition, hyperpolarization yields a $\sim 10^4$ -fold enhancement in sensitivity, which provides an essential benefit in comparison to conventional thermally polarized NMR.

References

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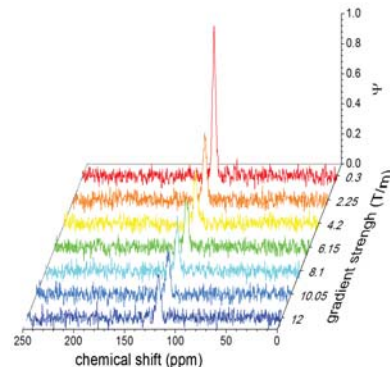


Fig. 2: ^{13}C spectra of CF_4 in aluminosilicate SWNT taken at different magnetic field gradients.

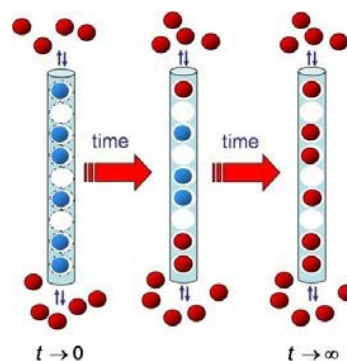


Fig. 3: Scheme demonstrating the tracer exchange experiment where labeling of the atom locations is facilitated by the large difference in the chemical shifts of adsorbed and gaseous Xe atoms.