Mixture diffusion of adsorbed organic compounds in metal-organic frameworks as studied by magic-angle spinning pulsed-field gradient nuclear magnetic resonance

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*New Journal of Physics* 13 (2011) 045016 (15pp)
Received 31 August 2010
Published 14 April 2011
Online at http://www.njp.org/
doi:10.1088/1367-2630/13/4/045016

**Abstract.** The magic-angle spinning (MAS) and pulsed-field gradient nuclear magnetic resonance (PFG NMR) techniques have been combined using a commercially available microimaging system providing a gradient in the magic-angle direction of up to $\pm 2.6 \text{ T m}^{-1}$, together with a narrow bore MAS probe. By narrowing the spectral linewidths, detection of the single and mixed molecular species adsorbed in porous material and their respective mobilities becomes possible. Here, we report on protocols for MAS PFG NMR measurements, new methods for the indispensable sample alignment along the MAS rotational axis and gradient direction and first experimental results of diffusion studies on $n$-hexane and benzene adsorbed in the metal-organic framework MOF-5.
1. Introduction

Pulsed-field gradient (PFG) nuclear magnetic resonance (NMR) [1, 2] and magic-angle spinning (MAS) [3] represent two established and widely applied techniques in NMR spectroscopy for the characterization of porous materials. While PFG NMR is generally used to investigate the translational motion of fluid-like phases, restricting influences of the inner surfaces of porous materials, MAS NMR is used to enhance the spectral resolution of the corresponding solid matrix and the fluid phases. The reduced mobility of adsorbed phases in porous materials leads often to an increased linewidth in the static NMR spectra, which makes it impossible to detect individual components in the sample by means of their chemical shift. The otherwise invaluable methods such as diffusion ordered NMR spectroscopy (DOSY; [4]) cannot be applied under these circumstances.

The first approaches to combine both basic techniques, MAS and PFG NMR, were those used by Cory et al [5] and Maas et al [6]. In the former arrangement, a gradient coil was wrapped around the spinner house and directed at the magic angle, to create a reference frame for solid-state imaging. Whereas in this setup modulated pulses were switched, the latter authors used time-independent gradients for the conduction of gradient spectroscopy as well as high-resolution MAS experiments, where solvent signals were suppressed by those means. As a result of those developments, a wide spectrum of applications emerged, ranging from the investigation of human cells [7] to diffusion studies in biophysics [8] and food science [9]. Furthermore, in more recent studies, diffusion in free liquids [10] and porous systems, such as zeolites [11, 12] and aluminum oxide tubes [13], were of particular interest for this PFG MAS method.

MAS PFG NMR used for the quantitative determination of diffusion coefficients is currently by no means standard in NMR studies. The aim of this work is to introduce and describe routines that are necessary for the combination of PFG and MAS techniques on a commercial NMR spectrometer equipped with the corresponding commercial components. Test procedures for alignment of the PFG and the MAS direction are introduced using a viscose polymer sample. Finally, the successful application of this method to study two-component
diffusion of $n$-hexane ($C_6H_{14}$) and benzene ($C_6H_6$) in the microporous metal-organic framework MOF-5 [14] is demonstrated.

2. Experimental

2.1. Hardware

For the MAS PFG NMR experiments, a Bruker Avance 400 spectrometer that operates at the proton resonance frequency of 400 MHz was used. As proposed in [12], a Bruker Micro 2.5 imaging probe providing pulsed magnetic field gradients with amplitudes of up to $G_{x,y,z,\text{max}} = \pm 1.5 \text{ T m}^{-1}$ in the $x$-, $y$- and $z$-directions is inserted into the room temperature bore of the superconducting magnet. This system is cooled by a continuous water flow at a constant temperature. A standard 4 mm $^1\text{H}/^{13}\text{C}$ narrow bore HR-MAS probe is attached. With this setup the influence of effects driven by the gradient pulses, such as mechanical distortions, is reduced compared to designs where the gradient coil is mounted directly on the stator. Moreover, with the MAS probe alignment along the space diagonal of the gradient system, an effective gradient strength of

$$|G_{\text{MAS},\text{max}}| = \sqrt{3} |G_{x,y,z,\text{max}}| = 2.6 \text{ T m}^{-1}$$

(1)

can be applied in the magic-angle direction by the simultaneous superposition of all three gradient directions. This is depicted in figure 1 together with the magic angle $\theta$. However, a drawback of this modular setup is that individual components (gradient and RF system) have to be properly aligned with respect to the shim system and $B_0$ before running the actual NMR experiment.

2.2. Sample alignment

As a first step, proper alignment of the four major components (homogeneous region of the $B_0$ field, shim, gradients and RF system) of the experimental setup had to be ensured. While the iso-centers of $B_0$ and shim coincide by magnet design, accurate positioning of the gradient and
RF systems with respect to each other as well as to the iso-center of $B_0$ needs to be ensured and adjusted when necessary.

To address this issue, a one-dimensional (1D) spin–echo imaging experiment [15, 16] was adapted to our needs with the pulse sequence depicted in figure 2. A Hahn-echo was extended by a static constant gradient $g_{\text{const}}$ throughout the whole sequence. By applying Fourier transform to the acquired data, the 1D spin density profile along the applied gradient direction is obtained and may be analyzed with respect to the actual position of the sample in the gradient reference system. When orientating the gradient $g_{\text{const}}$ in the $z$-direction, it is possible to match the center of the RF coil with the center of the gradient system by repeatedly acquiring individual scans (single scan mode) while physically moving the MAS probe in the gradient system up or down until the image is centered within the field of view. The same procedure applies for centering RF and gradient components together to the center of the shim coils. Here, the constant gradient was generated by the $z^1$ shim rather than by the gradient system, which allows for the alignment of the latter with respect to the former.

The most crucial point of the alignment procedure is to match the rotational axis of the sample (contained in the narrow bore MAS probe) to the magic-angle direction, which is a necessary standard procedure for MAS NMR experiments. In the case of MAS PFG NMR, however, the magic angle of the sample must also coincide with the direction of $G_{\text{MAS}}$ as generated by the gradient system. While this alignment of the sample is no issue in the non-spinning case, this step becomes indispensable for NMR diffusion measurements with a rotating sample. Artifacts will occur in the acquired NMR signal otherwise.

For this alignment, the MAS probe has two degrees of freedom within the gradient system. While there is no restriction for the azimuthal angle (the MAS probe can be rotated in the gradient system around the $z$-axis by 360°), a tilting mechanism in the MAS probe itself provides options to adjust the angle $\theta$ around the magic angle in the range of about 60° (see figure 3). Regardless of having the correct settings, each time the sample is changed, the spinner house must be tilted from the magic angle $\theta_{\text{MAS}}$ to the vertical, which requires the operator to repeat the alignment and prohibits the use of conventional methods for magic-angle alignment as proposed in the literature (e.g. [17]). To address this issue, the echo sequence in figure 2 is reused. A major advantage is that the proposed procedure does not rely on the presence of quadrupolar nuclei such as $^{79}\text{KBr}$ as used by Frye and Maciel [17] for magic-angle adjustment. The only condition is a sufficient signal-to-noise ratio of the sample in the single scan mode.

The projection of the sample in the MAS rotor onto the $x$–$y$ plane of the gradient system is measured as presented in figure 4. The criterion for a properly aligned MAS probe with...
Figure 3. The upper part of the used MAS probe with a spinner house containing RF coil and a sample aligned (a) with the magic-angle direction and (b) with the vertical.

Figure 4. Principle of sample alignment in the azimuthal direction. (a) A misaligned sample yields too a high profile (gradient along the target direction). (b) The sample is aligned properly and the profile is the flattest and longest. (c) Alternative indication of the optimum (narrowest and highest profile) is given when applying the gradient perpendicular to the target direction.

respect to its azimuthal position is a 1D image of the sample stretched to its maximum length (figure 4(b)) if the gradient is chosen to be $g_{\text{const}} = (g, -g, 0)$ in the three orthogonal directions. However, it is also possible to obtain the shortest image using a gradient $g_{\text{const}} = (g, g, 0)$ which is perpendicular to the target direction (see figure 4(c)). Very short $\pi/2$–$\pi$-echo intervals (of the order of 300 $\mu$s and less) are chosen in order to avoid potential signal loss for samples with short $T_2$-values.

To adjust the angle $\theta$ with respect to $B_0$, the gradient $g_{\text{const}}$ has to be altered accordingly. In figure 5, its direction is indicated. For the criterion of the shortest projection the resulting vector is $g_{\text{const}} = (-g, g, 2g)$. These alignment experiments have been tested with a $^{79}$KBr sample, spinning at 5 kHz, which allowed us to monitor the results of the gradient-based alignment by means of the acquired $^{79}$KBr spectra (figure 6).
Figure 5. Direction of the applied constant gradient for alignment of the sample with respect to $B_0$. 

(\textbf{a}) Overview in 3D coordinates \hspace{1cm} (\textbf{b}) Extraction of coloured layer in (\textbf{a})

Figure 6. Monitoring the angle setting as obtained by experiments based on figure 2 using the $^{79}$KBr sample.

Both the $x$–$y$ and the $\theta$ alignment are alternately conducted in iterations until any adjustment of the MAS probe direction no longer improves profiles. Typical absolute amplitudes of the constant gradient used for the adjustment are of the order of 50 mT m$^{-1}$. A comparison of the proposed method with the conventional procedure using the quadrupole nucleus $^{79}$KBr yields an angle deviation of less than 0.2°, which is more than sufficient.

2.3. Temperature calibration

For MAS NMR experiments, it is well known [18] that, due to frictional heating, the sample temperature depends on the spinning frequency. van Geet [19] showed that this temperature may be determined by means of NMR experiments. The so-called NMR thermometer uses the difference $\Delta \nu$ of the OH- and CH$_3$-groups of methanol to trigger changes in the amount of hydrogen bonding depending on the temperature $T_{\text{sample}}$, thus shifting the OH-peak. By means of the empirical equation from [19], adapted for the $^1$H resonance frequency of 400.13 MHz,
the dependence of $T_{\text{sample}}$ on the rotational speed becomes easily accessible (figure 7):

$$T_{\text{sample}}(\Delta \nu) = 435.5 - 0.178 \, 89 |\Delta \nu| - 6.5882 \times 10^{-5} |\Delta \nu|^2.$$  \hfill (2)

As a matter of fact, the variation from 3 to 10 kHz causes a nonlinear step-up in temperature of up to 9 K. It also becomes evident that besides the ambient temperature given by the bearing pressure (constant at $\approx 24.5 \, ^\circ\text{C}$), which flows directly against the sample, also the temperature of the gradient system plays an important role, even though it is farther away with no direct connection to the rotor. However, all deviations are quite moderate for spinning frequencies of 5 kHz as used for this work.

2.4. Samples

For first calibrations as well as for initial diffusion measurements, a neat high-vacuum grease sample was prepared, which has a sufficiently high viscosity and low diffusivity that its spin–echo NMR signal intensities are not reduced by diffusion in inhomogeneous magnetic fields. The $^1\text{H}$ NMR spectrum shows two major lines, which are separated by 0.4 ppm. Relaxation times $T_1$ and $T_2$ are well above 500 ms, which allows us to test the system in a static and MAS setup with high signal-to-noise ratios. Furthermore, due to its high viscosity, possible effects resulting from the sample rotation, such as convection, are reduced to a minimum.

As the actual target system, diffusion studies were to be conducted for a mixture of $n$-hexane and benzene adsorbed in the metal-organic framework MOF-5. This type of framework is quite a new class of porous material, which was introduced by the group of Yaghi [20] and refined regarding the synthesis process and quality by Eddaoudi et al [21]. The MOF-5 crystals were filled into a 3 mm glass tube that fits in 4 mm MAS rotors and were slowly heated to $T = 393 \, \text{K}$ in order to remove residual components from the synthesis and storage, such as solvents and water. After activation, the powder was cooled down and frozen in liquid nitrogen, where it was exposed to the desired amount of adsorbates. For the present study, MOF-5 was subsequently loaded with $n$-hexane and benzene. The final loading was 13 benzene molecules and 15 $n$-hexane per unit cell. The sample was kept at room temperature for 1 day.
2.5. Gradient properties

Before the first diffusion experiments were conducted, the gradient system was extensively explored regarding safe and optimum settings under spinning conditions ($\nu_{\text{rot}} = 5 \text{ kHz}$). In particular, this included the determination of the strength of eddy currents that are known to heavily compromise the quality of NMR measurements (see e.g. [22, 23]).

To estimate the influence of eddy currents, a simple experiment was set up, using a single gradient pulse of preselected strength at a variable distance $\tau$ from an excitation pulse (figure 8). In the ideal case, the free induction decay (FID) should not be affected for any chosen value of $\tau$.

As indicated in figure 9, for a sinus gradient shape with $\delta = 3 \text{ ms}$ and a peak value of 2.6 T m$^{-1}$, only for large time gaps between the gradient and $\pi/2$ pulse, the NMR spectrum of the vacuum grease remains unaffected. A detailed analysis shows that minor distortions occur for about $\tau = 15 \text{ ms}$ and less. For very small distances ($\tau < 5 \text{ ms}$), the phase also starts to shift. For a gradient length of $\delta = 0.5 \text{ ms}$, the above times for $\tau$ are quite similar, but with stronger effects when setting shorter values. Consequently, steep gradient slopes are likely to cause more severe mechanical and electronic distortions, resulting in corrupt NMR data, when violating the secure distances of $\tau$. This behavior is consistent and reproducible for all considered samples.

Another important precondition is the gradient uniformity—and along with it—the accuracy, namely the matching of all applied gradient pulses [2]. As outlined in [2, 24], the introduction of read gradient blocks facilitates the determination of possible gradient mismatches, which then would be reflected in echo shifts in the time domain. Therefore, as shown in figure 10, a stimulated echo experiment equipped with PFGs was extended by two...
Figure 10. Adapted NMR pulse sequence for time domain diffusion measurements.

Figure 11. Echoes in the time domain acquired with a sample of vacuum grease rotating at 5 kHz.

static gradients $g_{\text{read}}$ in the interval after excitation and during acquisition, respectively (see [24] for details).

Using the pulse sequence of figure 10 and raising the gradient pulses $G$ up to their maximum value of 2.6 T m$^{-1}$ did not result in any significant echo shift in the time domain for various setups and samples (see e.g. figure 11 for vacuum grease, $\delta = 7$ ms, $\Delta = 500$ ms). The absence of any noticeable echo shifts in the time domain under the application of read gradients proves that no gradient mismatch is occurring for the given NMR system and the parameters chosen.

In summary, to guarantee the reliability of diffusion experiments using this special setup, it is strongly recommended to always run the frequency-resolved measurements in conjunction with the time domain experiments using similar measurement parameters.

3. Results

3.1. Vacuum grease test sample

For first proof-of-principle experiments, the vacuum grease was used as a basic and highly viscous sample. Thus as outlined above, perturbations resulting from convection due to fast
sample rotation and potential temperature gradients are precluded, while still having diffusion in the bulk phase.

The measurements under MAS PFG NMR conditions were carried out using an observation time of \( \Delta = 500 \text{ ms} \). The pulsed magnetic field gradients of \( \delta = 4.5 \text{ ms} \) in length (half-cycle of a sinus wave) were raised up to \(|G| = 2.6 \text{ T m}^{-1}\). Under these conditions experiments have been conducted, considering safe settings for \( \tau \) under sample rotation at 5 kHz in the time domain (shown in figure 10) as well as in the frequency domain, omitting the read gradients in the latter case.

Additionally, static PFG NMR time domain experiments were conducted with the home-built FEGRIS NMR spectrometer [2, 24]. In order to have comparable \( b \)-values (containing all parameters controlled by the experiment as \( (\gamma \delta G)^2 (\Delta - \frac{\delta}{2}) \) with \( \delta \) being the gradient duration, \( G \) the gradient amplitude, \( \Delta \) the observation time and \( \gamma \) the gyromagnetic ratio), the gradient width was adjusted taking into account different gradient shapes.

Regardless of the loss of information about a single species, the integration over the whole spectrum allows direct comparison to the time domain data. A joint representation of the processed data after normalization (figure 12) confirms the feasibility of the MAS PFG NMR method. This conclusion is supported by the proper alignment of all echoes in the time domain (see figure 11), indicating matched PFGs throughout the experiments. Furthermore, the comparison between static and rotating samples proves that no additional artifact is introduced due to sample spinning. Please also note that the obtained diffusion coefficients are of the order of \( 10^{-13} \text{ m}^2 \text{ s}^{-1} \), emphasizing the potential usefulness of the hardware for the investigation of slow diffusion processes.

### 3.2. n-hexane and benzene in MOF-5

We extended the test of the MAS PFG NMR system by studying the single component diffusion of benzene adsorbed in the microporous host material MOF-5. Spin–echo attenuations were acquired using time and frequency domain NMR experiments as proposed above at an observation time of \( \Delta = 40 \text{ ms} \). The data fit well to a biexponential behavior (\( D_1 \) and \( D_2 \)), which
Figure 13. Spectrum of a mixture of \( n \)-hexane and benzene adsorbed in MOF-5 (solid line) together with the corresponding isolated peaks (dashed lines) resulting from a line deconvolution.

has already been observed for a number of hydrocarbons in MOF-5 [25]. Furthermore, the diffusion coefficients \( D_1 = 2.36 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) and \( D_2 = 3.13 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \) are comparable to those determined by means of earlier static PFG NMR time domain experiments [26] and agree well with data obtained by MD simulations [27, 28] at room temperature. The remaining differences between the experimental data may be attributed to the fact that separate samples were prepared for the static and MAS PFG measurements, resulting in variation of the diffusivities due to differences in the loading.

While those studies prove the feasibility of the hardware and its accurate performance, the more relevant case that taps the full potential of the MAS PFG NMR method is the investigation of the mixture of benzene and \( n \)-hexane adsorbed in the framework.

The corresponding \(^1\text{H} \) MAS NMR spectrum at 5 kHz (figure 13) shows three distinct regions. The two narrow peaks at 0.9 and 1.2 ppm are assigned to the \( n \)-hexane, whereas the peak at 7.2 ppm refers to the adsorbed benzene. The signal from the lattice phenyl groups occurs at around 8.6 ppm as a broad region.

Transversal relaxation times for the sample under study were found to be comparably short with \( T_{2,n\text{-hexane}} = 15 \text{ ms} \) and \( T_{2,\text{benzene}} = 8 \text{ ms} \), respectively, which might be a consequence of an insufficient washing process during synthesis of the crystals. Recalling the safe distances for the gap between the gradient pulse and the acquisition window of about 15 ms, the setup of an appropriate diffusion experiment became challenging. As a compromise, this gap was reduced to 6 ms by checking for distortions that are still negligible while having sufficient NMR signal. The observation time was chosen to be \( \Delta = 100 \text{ ms} \) for a pulsed gradient length of \( \delta = 0.5 \text{ ms} \). Gradient amplitudes were raised to the maximum of 2.6 T m\(^{-1}\).

Since parameters in timing and gradient strengths are chosen to be close to the experimental limit, a slight phase shift of up to 20\(^\circ\) occurs with increasing gradient amplitudes. By means of a zeroth-order phase correction, this shift was eliminated individually for each gradient step. Motivated by the fact that for the corresponding time domain experiment any significant echo shift is absent and thus gradients are applied accurately, this procedure is legitimized.

However, the rigid lattice at 8.6 ppm does not appear in the acquired MAS PFG spectrum due to very short relaxation times. An integration over the separated peaks of \( n \)-hexane
Table 1. Summary of the results of MAS PFG NMR experiments for the mixture of $n$-hexane and benzene adsorbed in MOF-5.

| Component  | $p_1$  | $D_1$ ($10^{-10}$ m$^2$ s$^{-1}$) | $D_2$ ($10^{-10}$ m$^2$ s$^{-1}$) |
|------------|--------|---------------------------------|---------------------------------|
| $n$-Hexane | 0.22   | 9.49                           | 0.95                            |
| Benzene    | 0.14   | 9.09                           | 0.83                            |

Figure 14. Attenuated NMR signals for the MOF-5 sample. (a) Spectrum dependence on the applied gradient. (b) Signal attenuation for benzene (open symbols) and $n$-hexane (full symbols) selectively derived from the spectrum in (a).

and benzene, respectively, yields again biexponential slopes for all components, from which diffusion coefficients were obtained with the help of the equation

$$M(b)/M(0) = p_1 \exp\{-bD_1\} + (1 - p_1) \exp\{-bD_2\}.$$  (3)

The results (including the relative amounts of the fast component $p_1$) are given in table 1. The mean diffusion coefficients (thus integrating all the spectra without selecting individual peaks) agree well with corresponding values obtained by time domain experiments.

Diffusion coefficients (with respect to $D_1$ in table 1) for benzene agree well with those reported by Hertel et al [26] for the respective loading. Furthermore, diffusivities for $n$-hexane decrease by a factor of 4 as compared to the experiments in [25] and MD simulations in [29]. This may be attributed to the higher loading and the higher occupation of space in the MOF related to it. Hence, compared to the bulk phases of the two molecule species ($n$-hexane: $4.26 \times 10^{-9}$ m$^2$ s$^{-1}$; benzene: $2.21 \times 10^{-9}$ m$^2$ s$^{-1}$ [30]) a total drop by a ratio of 4.5 for $n$-hexane and a ratio of 2.4 for benzene is observed, respectively.

In the spectrum shown in figure 14(a) an additional signal appears at about 0.6 ppm, which is hidden under the shoulder of the rightmost $n$-hexane peak for small $b$-values. With increasing $b$-value it does not show significant attenuation. Most likely, this component indicates the presence of additional hydroxyl groups, which might be situated at the glass surface of the sample tube.

New Journal of Physics 13 (2011) 045016 (http://www.njp.org/)
4. Conclusion

NMR experiments using PFG and MAS techniques have been successfully combined for the investigation of motional behavior of single and mixed hydrocarbons in the metal-organic framework MOF-5. A conventional narrow-bore MAS probe was attached to a commercially available micro 2.5 imaging system, providing gradient amplitudes of up to $\pm 1.5 \text{ T m}^{-1}$ in each direction, which being super-positioned results in an effective strength of up to $\pm 2.6 \text{ T m}^{-1}$ in the magic-angle direction.

It was shown that with the help of a 1D imaging sequence, the gradient and RF part of the spectrometer can be easily aligned with each other. The tests for providing safe parameters for diffusion measurements showed that the time between pulsed gradient and the acquisition in any sequence may not be less than 15 ms to avoid the potential influence of decaying distortions resulting from the gradients. However, smaller delays are possible if the measurement is evaluated by corresponding time domain experiments and data. The gradient uniformity was approved by time domain measurements involving the application of a read gradient during acquisition and its corresponding balance in standard diffusion sequences. Moreover, those time domain measurements are found to be advisable for each individual NMR diffusion experiment using spectral resolution for this setup.

Resulting from first tests and consistency checks, diffusion coefficients as low as $10^{-13} \text{ m}^2 \text{ s}^{-1}$ were obtained using the example of high-vacuum grease, which agree well with static measurements.

Finally, the application of the present setup to the study of diffusion of a mixture of $n$-hexane and benzene adsorbed in MOF-5 was demonstrated. The obtained diffusivities for individual molecular species as published in the literature so far were reproduced and verified, rendering possible DOSY studies in adsorbate/adsorbant systems with short transverse relaxation times. Such multicomponent diffusion studies in MOFs by MAS PFG NMR are interesting, because adsorbed fluid molecules move through the force field of the porous host, probing in this way fundamental host–guest and guest–guest interactions. This provides valuable information about the application of MOFs in heterogeneous catalysis and separation.

Acknowledgments

We acknowledge S Amirjalayer and R Schmid (Ruhr-University Bochum, Germany) for the synthesis of MOF-5. We thank the Deutsche Forschungsgemeinschaft (DFG) for funding via the IRTG ‘Diffusion in porous materials’ (GRK 1056/2) and the SPP 1362 ‘Poröse metallorganische Gerüstverbindungen’, STA 648/1-1. MG thanks the Max-Buchner Foundation for funding. Financial support from New Zealand Centres of Research Excellence Fund and New Zealand Foundation for Research, Science and Technology is acknowledged by PG. We also thank Bruker for support while configuring the setup.

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