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^{1}H NMR signal broadening in spectra of alkane molecules adsorbed on MFI-type zeolites

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ABSTRACT

The anisotropic behavior of C_1–C_6 alkane molecules adsorbed in MFI zeolite was studied by ^{1}H nuclear magnetic resonance (NMR) using single-pulse excitation, Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence, Hahn echo (HE) pulse sequence, and magic-angle spinning. The molecular order parameter was obtained by both static ^{2}H NMR spectroscopy and molecular simulations. This yields an order parameter in the range of 0.28–0.42 for linear alkanes in MFI zeolite, whereas the parameter equals zero for FAU zeolite with a cubic symmetry. Thus, in the case of a zeolite with a non-cubic symmetry like MFI, the mobility of the molecules in one crystallite cannot fully average the dipolar interaction. As a consequence, transverse nuclear magnetization as revealed in the echo attenuation notably deviates from a mono-exponential decay. This information is of particular relevance for the performance of pulsed field gradient (PFG) NMR diffusion experiments, since the occurrence of non-exponential magnetization attenuation could be taken as an indication of the existence of different molecules or of molecules in different states of mobility.

1. Introduction

Isotropic mobility of molecules adsorbed in zeolites should completely average out spin interactions which cause line broadening in nuclear magnetic resonance (NMR) spectroscopy of solids. Additional application of magic-angle spinning (MAS), Hahn echo (HE) or Carr–Purcell–Meiboom–Gill (CPMG) pulse sequences can reduce the effective line broadening in such systems. This is essential for pulsed field gradient (PFG) NMR experiments, since the cutback of line broadening corresponds to a prolongation of the effective transverse relaxation time T_2^*, which increases the sensitivity of NMR diffusometry. As a consequence, short relaxation times limit the duration of the gradient pulses in PFG NMR.

A serious problem arises, if the echo decay envelope measured by HE or CPMG pulse sequences is not mono-exponential and seems to consist of a superposition of a fast and a slowly decaying component of the signal [1]. Such a relaxation behavior is of twofold relevance for the performance of PFG NMR. First, the signal intensity is found to be notably decreased with increasing pulse spacing. However, large spacing between the radio frequency pulses is indispensable for the application of field gradients with large pulse widths. They are inevitable for the measurement of small diffusivities and/or displacements [2–4]. Hence, when applying PFG NMR to diffusion measurements with such systems, one has to find a compromise between sufficiently large signal intensity and the application of field gradients of sufficiently large pulse width.

As a second, even more important feature, a transverse relaxation including several contributions reveals attenuation curves notably deviating from mono-exponential behavior. Such a situation is typical of systems accommodating molecules of different mobility [5]: (i) a small fraction of highly mobile molecules with a long transverse relaxation time giving rise to a slowly decaying part at large observation times, (ii) a major fraction of less mobile molecules the contribution of which to the signal rapidly decreases, with increasing observation time as a consequence of the much shorter relaxation time. In this case, application of PFG NMR would provide the diffusivity of the small fraction of highly mobile molecules rather than that of the major fraction of the molecules

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[6]. We shall demonstrate in the present study that in the case of non-cubic symmetry, like in MFI-type zeolites, the deviation from mono-exponential echo decay is caused by the dipolar interaction of the ^{1}H nuclei of the diffusants which is not averaged out completely for some systems with confined geometry.

2. Experimental

Silicalite-1 (all-silica MFI zeolite) with a crystallite size in the range from $10\,\mu m \times 10\,\mu m \times 100\,\mu m$ to $20\,\mu m \times 20\,\mu m \times 200\,\mu m$ were obtained from synthesis gels containing tetrapropylammonium bromide (TPABr, 98%, Aldrich) as the structure-directing agent, Ludox AS 40 (Aldrich) as the silicon source, de-ionized water as the solvent, and ammonia solution (32%, Aldrich) for pH adjustment. The molar composition of the reaction gel was $(TPA)_2O$:10.8 SiO_2:32 $(NH_4)_2O$:310 H_2O [7]. Crystallization was carried out in Teflon-lined autoclaves which were heated to 453 K and kept at this temperature for 5 days. The resulting crystalline products were filtered off and washed with de-ionized water. After washing, the crystallites were kept in 0.1 M NaOH solution at room temperature for 1 day to remove amorphous residues. The crystallites then were filtered off, washed, and dried at room temperature. For template removal, the crystallites were heated to 823 K with a heating rate of $0.5\,K\,min^{-1}$ and kept at this temperature for 10 h in ambient air.

The zeolite Na-X (FAU-type zeolite) was provided by Dr. Xiaobo Yang, University of Hannover. It has a crystallite size of about $50\,\mu m$ and a silicon-to-aluminum ratio of 1.2. The samples for the NMR measurements were prepared by heating 20 mg of the zeolite sample in glass tubes of 3 mm outer diameter. The temperature was increased under vacuum at a rate of $10\,K\,h^{-1}$ and then the samples were maintained at 673 K for 24 h under vacuum (less than 10^{-2} Pa). The zeolite Na-X was loaded with 16 butane molecules per unit cell. Silicalite-1 was loaded with 4 methane, 8 ethane, 4 *n*-butane, 4 isobutane, or 4 *n*-hexane molecules per unit cell. Then the glass tube (8 mm length) was sealed off. NMR experiments were carried out at room temperature.

^{1}H NMR experiments were performed on a Bruker AVANCE spectrometer operating at 400 MHz with a wide-bore magnet. Selected measurements presented in Figs. 1 and 4 were done on a Bruker AVANCE 750 spectrometer, in order to investigate the field dependence of the spectra. MAS was usually performed at $\nu_{rot} = 10$ kHz. The typical $\pi/2$-pulse length was $2.5\,\mu s$. The relaxation delay of 1 s was longer than the longitudinal relaxation times. For CPMG measurements [8] we used a single-echo acquisition after an even number of π-pulses. The CPMG decay was obtained from five echo measurements. The decay of the HE envelope [9] shows multi-component behavior. Using the last two points of the decay, we can define a relaxation time T_2^{HE} which corresponds to the slowly decaying component of the echo. A fast decaying component of the echo envelope can be described by a transverse relaxation time near the relaxation time T_2^{FID} which corresponds to the free induction decay (FID). Static ^{2}H NMR spectra were obtained at 61.4 MHz by means of a quadrupole echo [10]. Inversion recovery was used, in order to observe selectively the CD_3 and CD_2 groups. The signal intensity of CD_3 group was zeroed at pulse spacing (between first π-pulse and following $\pi/2$-pulse) of $\tau_{IR} = 192$ ms. The CD_2 groups were zeroed at $\tau_{IR} = 70$ ms [10].

3. Results

3.1. Static ^{1}H NMR

Spectra were measured in the field of 17.6 and 9.4 T without MAS (static spectra), in order to determine the field-dependent broadening. Fig. 1 shows the spectra. In addition to the solid 400-MHz signal and the dashed 750-MHz signal, the dotted line is the downscaled (400/750) 750-MHz signal. The line broadening for isobutane in silicalite-1 is proportional to the external magnetic field. But line broadening for *n*-butane in silicalite-1 appears to be field independent, whereas the same molecule in zeolite Na-X exhibits pure field-dependent broadening. A pure field-dependent broadening could also be observed for methane in silicalite-1, whereas n-hexane behaves similar to n-butane. Field-dependent inhomogeneous broadening is caused by chemical shift anisotropy, by distribution of isotropic values of the chemical shift, and by susceptibility effects. For dominant dipolar interaction, however, line broadening would remain unaffected by the magnetic field. Thus, the coincidence of the spectra directly measured at 400 MHz and those downscaled from 750, indicates that inhomogeneous broadening seems to be the dominant effect for isobutane in silicalite-1 and also for *n*-butane in zeolite Na-X. By contrast, dipolar interaction is not completely averaged out by the mobility of the n-butane molecules in a crystallite of silicalite-1.

Figs. 2 and 3 show that HE and CPMG pulse sequences significantly prolongate the transverse relaxation in comparison with the FID. Some NMR broadening effects like chemical shift anisotropy, heteronuclear dipolar interaction and sample susceptibility should be averaged out by HE or CPMG, but homonuclear dipolar interactions should remain. Relaxation times T_2^{CPMG} can be determined from the slopes of the decays in Fig. 3. These values are found to depend slightly on the pulse spacing 2τ (by a factor of about two or less), except for *n*-butane in Na-X, where T_2^{CPMG} is found to decrease from 108 ms ($\tau = 10\,\mu s$) to 10 ms ($\tau = 500\,\mu s$). As an important message of this figure, the extrapolation of the decay curves to 0 ms often fails to meet the intensity of 100%. The value 100% is referred to the intensity of an echo after a pulse train $\pi/2$, τ, π, 2τ, π, τ with $\tau = 10\,\mu s$, which eliminates the disturbing effect caused by the inhomogeneity of the radio frequency field. This effect is not observed for *n*-butane in Na-X. But for the silicalite-1 sample loaded with *n*-butane, e.g., by extrapolating to 0 ms, we obtain relative intensities of 100% for $\tau = 10\,\mu s$, 90% for $50\,\mu s$, 59% for $100\,\mu s$, 36% for $250\,\mu s$, and 17% for $\tau = 500\,\mu s$.

Fig. 2 shows strong deviations from the mono-exponential decay of the plotted echo envelope. The intensity of the HE after the ($\pi/2$, τ, π, τ) pulse sequence is given as a function of $t = 2\tau$. By fitting the experimental data to a two-exponential decay, only 20% of the ethane and butane signal intensity is found to belong to the slowly decaying component.

CPMG echo intensities after a $\pi/2, (\tau, \pi, 2\tau, \pi, \tau)_n$ pulse sequence show a similar behavior. In Fig. 3 we have for $\tau = 500\,\mu s$ all even echo amplitudes with $n = 1, 2, 3, 4$, and 5, whereas for $\tau = 10\,\mu s$ only the intensities for $n = 50$, 100, 150, 200, and 250 were measured. Therefore, we observe in Fig. 3 for the time $t \geqslant 2$ ms only the slowly decaying component of the signal.

Table 1 summarizes the different time constants T_2 of the magnetization decays in Figs. 2 and 3. In comparison with the time constant of the FID, T_2^{FID}, application of MAS, of the CPMG pulse sequence or of a HE provide a drastic prolongation of T_2 of alkane molecules for zeolite types like FAU, which belong to a cubic symmetry group. By contrast, under the influence of a non-cubic symmetry like MFI significantly shorter relaxation times are obtained.

3.2. ^{1}H MAS NMR

Fig. 4 shows the ^{1}H MAS NMR spectra of isobutane and *n*-butane in silicalite-1 obtained with a MAS frequency of 10 kHz. At 400 MHz and for $\nu_{rot} = 10$ kHz we have a full-width-at-half-maximum (fwhm) of the methyl signal of 0.13 ppm (*n*-butane)

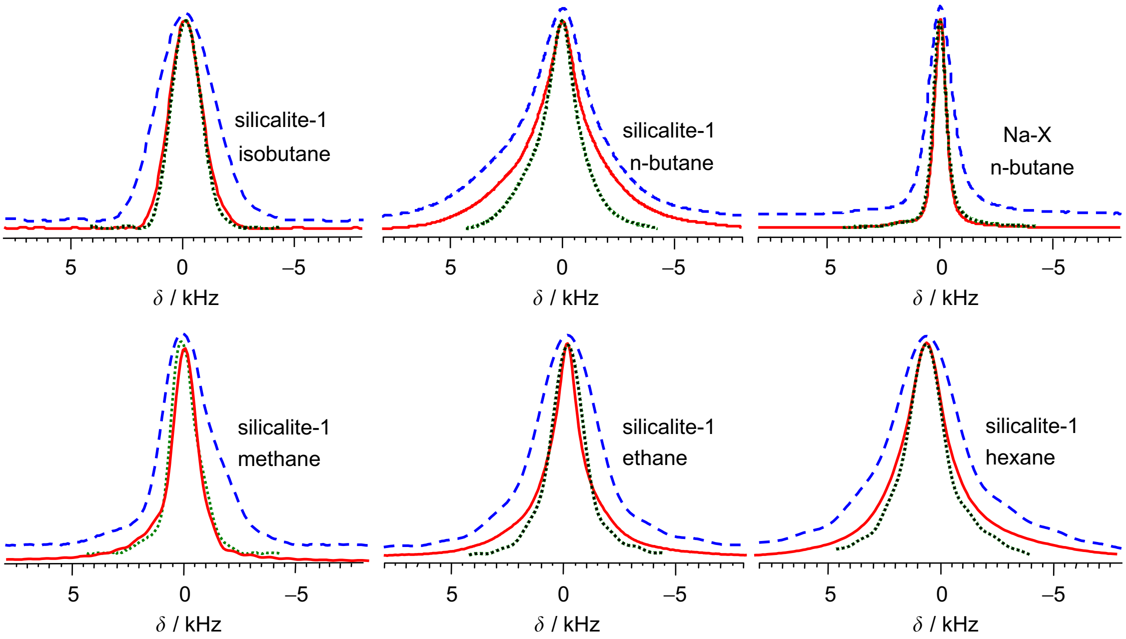

Fig. 1. Static ^{1}H NMR spectra obtained without magic-angle spinning at 750 MHz, dashed lines (- - -), and 400 MHz, solid lines (—). The dotted lines (• • •) denote the downscaled (400/750) 750-MHz signals.

and 0.34 ppm (isobutane), and for $\nu_{\mathrm{rot}} = 3$ kHz of 0.16 and 0.41 ppm. It means that the rotational frequency has a weak influence on the linewidths. At 750 MHz and $\nu_{\mathrm{rot}} = 10$ kHz we obtained a fwhm of 0.06 ppm for *n*-butane and of 0.26 ppm for isobutene in agreement with previous MAS PFG NMR studies [11,12] MAS PFG NMR. This means that we have a significant narrowing of the linewidths going from 400 to 750 MHz. The decrease of the fwhm in the ppm scale with increasing field shows that a distribution of isotropic values of the chemical shift is very small and has no dominant influence on the ^{1}H NMR linewidth.

3.3. Static ^{2}H NMR

First-order quadrupole broadening of deuterium spectra gives usually a Pake's doublet [13]. Without motional narrowing, the spectrum of alkane C–D-bonds should show a spacing of the maxima corresponding to 3/4 $C_{\mathrm{qcc}} = 120$–130 kHz and $\eta \approx 0$, where C_{qcc} denotes the quadrupole coupling constant and η is the asymmetry parameter [14]. Isotropic mobility reduces the line spacing to zero. Anisotropic mobility causes a reduction of the line spacing and a larger asymmetry parameter. The quadrupole coupling constant is reduced by the geometry factor $(3\cos^2\beta{-}1)/2$, where β denotes the angle between the C–D-bond axis and the rotational axis. For the tetrahedral geometry of the CD_2 groups we have $\beta \approx 109.47^\circ$ and the factor becomes 1/3. Then, for fast internal rotation without restriction, we expect 3/4 $C_{\mathrm{qcc}} = 40$–43 kHz. We still expect a rotation around the channel axis if fast trans-gauche isomerization inside the channel is hindered by the channel geometry. Then we have $\beta \approx 90^\circ$ and the factor becomes 1/2 and 3/4 $C_{\mathrm{qcc}} = 60$–65 kHz. For the CD_3 groups, an additional rotation gives rise to the factor 1/9 and 3/4 $C_{\mathrm{qcc}} \approx 14$ kHz is expected [14].

Fig. 5 shows a stronger line broadening of CD_2 groups corresponding to their more hindered rotation. We focus on the CD_2 groups which cannot freely rotate like the CH_3 groups and which are thus more representative for the mobility of the molecule. Nevertheless, a fast rotation of the CD_2 group about their C_3 axis in the central C–C bond (trans-gauche isomerization) or a rotation about the channel axis should take place. It reduces the line broadening by a factor 1/3 or 1/2, see above. So we expect a line spacing of 3/4 $C_{\mathrm{qcc}} = 41.5 \pm 1.5$ kHz for a freely rotating molecule or of 3/4 $C_{\mathrm{qcc}} = 62.5 \pm 2.5$ kHz for a molecule rotating about one molecular axis which is kept parallel to the channel axis. The spacing goes to zero, if the molecular axis realigns isotropically in the zeolite crystallite. If the reorientation is not isotropic, the averaging can be described by the order parameter $(3\cos^2\Theta{-}1)/2$, where Θ denotes the angle between the molecular axis and any chosen crystallographic axis. From the experimentally observed line spacing 17.25 kHz in the ^{2}H NMR spectrum of CD_2 groups, with respect to the free trans-gauche isomerization we got an order parameter of $17.25/41.5 \approx 0.42$ or -0.42. With respect to the free rotation in the channel we have $17.25/62.5 \approx 0.28$ or -0.28. The sign is not definite.

3.4. Molecular conformations and order parameters determined from simulations

The order parameter was obtained also by configurational-bias Monte Carlo (CBMC) simulations of equilibrium loading and conformation of the molecules in the zeolites. In the CBMC simulations the zeolite lattice are assumed to be rigid. The adsorbate molecules are described with a united atom model [15]. The interaction between adsorbed molecules is described with Lennard–Jones terms, bond stretching terms, bond bending terms and torsion terms. The adsorbate–zeolite interactions have been modeled through Lennard–Jones terms, taking only the oxygen atoms of the zeolite into account. Force field parameters were taken from Dubbeldam et al. [16]. Each simulation started with insert moves to obtain the desired loading. After an equilibration period (1000 cycles), 100,000 cycles were performed. Each 1000 cycles, the order parameter was sampled by considering a straight line through the first and last pseudo-atom of each molecule. The order parameter was averaged over all samples to obtain the values shown in Fig. 6.

Again Θ denotes the angle between any chosen crystallographic axis and the molecular axis which is defined by the positions of the two terminal carbon atoms. For *n*-butane in the FAU zeolite which has a cubic symmetry we obtain the expected

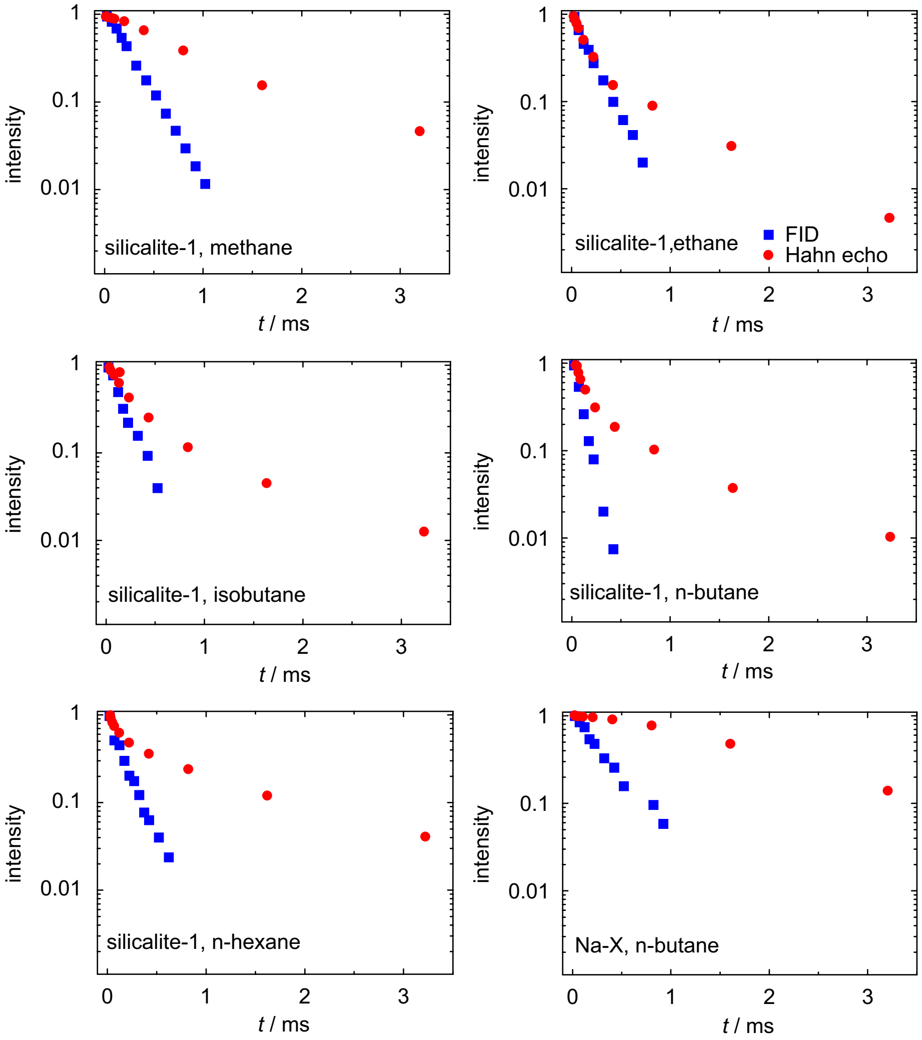

Fig. 2. Plot of the free induction decays (■) and the Hahn-echo decays (●) of the ^{1}H NMR signals by applying Hahn-echo pulse sequences with different $\pi/2-\pi$-pulse distances $20\,\mu s \leqslant \tau \leqslant 1600\,\mu s$.

order parameter near to zero. The variance with respect to zero is 0.005 for all loadings up to 8 molecules per cavity or 48 per unit cell. But for a loading of 1 *n*-butane molecule per crossing (or 4 butane molecules per unit cell) in silicalite-1, an order parameter of $\Theta = -0.33$ is obtained. This is in the range 0.28–0.42 obtained by ^{2}H NMR. For *n*-hexane in MFI, the order parameter obtained from simulations is $\Theta = -0.40$.

4. Discussion

The static ^{1}H NMR lineshapes show a residual dipolar broadening for linear molecules in zeolite silicalite-1, whereas the effect is missing for linear molecules in the cubic symmetry of FAU zeolite as well as for non-linear molecules in MFI zeolites.

CPMG and HE pulse sequences prolongate the transverse relaxation significantly with respect to the application of a single pulse. But, for linear molecules in MFI zeolites, the transverse relaxation decays, as measured by means of CPMG or HE, strongly deviate from a mono-exponential behavior. This can be explained by a strong anisotropy of the transverse relaxation under the influence of homonuclear dipolar interaction.

The quadrupolar ^{2}H NMR line broadening and snapshots of molecular simulation can be explained by an order parameter in the range of 0.28–0.42 for linear alkanes in the MFI-type zeolite. These facts allow the conclusion that the deviation of the NMR echo envelope from a mono-exponential decay does not indicate the existence of different molecular species with different mobility. It may rather be explained by the effect of nuclear magnetic relaxation.

The mobility of linear molecules in a confined environment can be anisotropic. For example, compared to the immobile molecule, very fast rotation of linear *n*-alkanes around one rigid axis reduces the NMR linewidth by a factor of two. In the case of fast isotropic rotation, however, the linewidth should be reduced to zero.

Anisotropy of the mobility should not be expected to occur for methane in any zeolite, nor for linear *n*-alkanes in zeolites such as FAU that have cubic symmetry. For the latter, the molecule jumps between different adsorption sites in such a way that the molecular axis takes all orientations with respect to the external magnetic field with the same probability. This averages out all intramolecular dipolar interactions. *n*-Alkanes in silicalite-1, however, are accommodated by a channel systems which does not provide cubic symmetry. In other words, molecular orientation in one crystallite is not isotropically distributed. The linewidth of completely immobilized alkane molecules amounts to some 10 kHz. Molecular motion leads to line narrowing. However, even slight deviations from cubic symmetry in the molecular orientations can cause a residual dipolar linewidths of the order of as much as 1 kHz. This is the situation shown in Fig. 1.

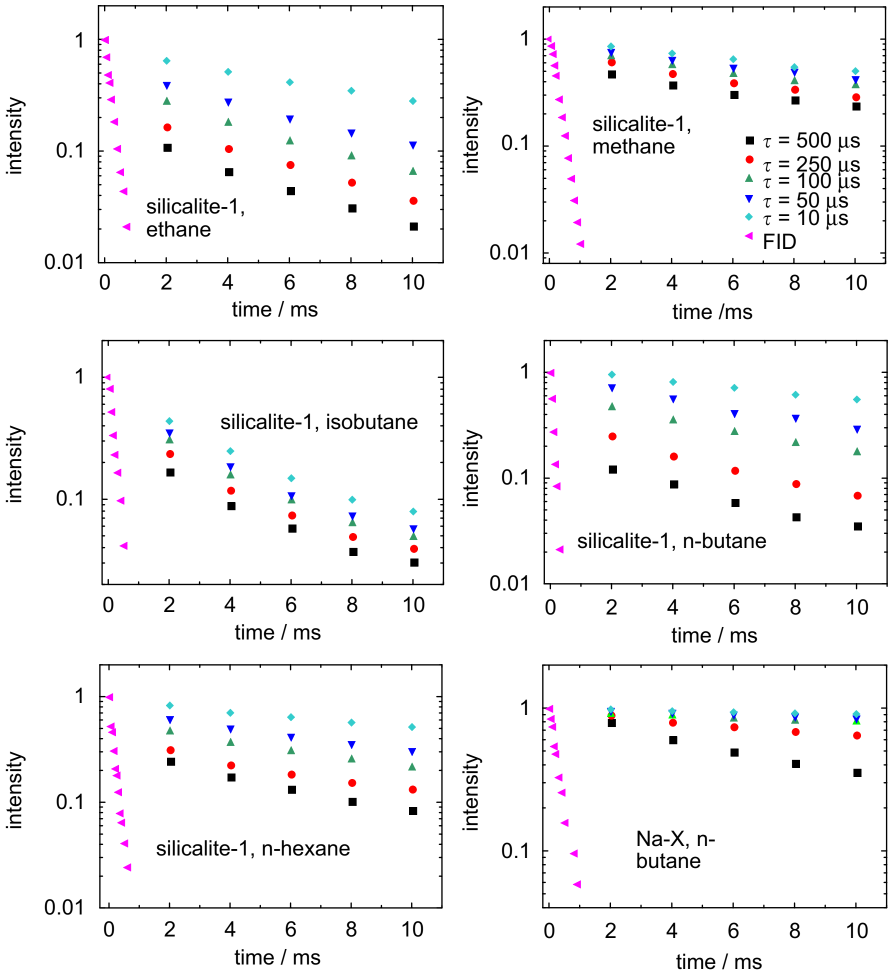

Fig. 3. Plot of the free induction decays (FID, ◀) and the echo decays of the ^{1}H NMR signals by applying CPMG pulse sequences with π-pulse distances 2τ varying from 20 µs (◆) to 1000 µs (■) for different adsorbate–adsorbent systems as indicated in the representations. The legend for the symbols used for the various distances are indicated in the top right graph. Observation times range from 0 to 10 ms.

Table 1
Transverse relaxation times T_2 of adsorbed alkane molecules in the considered host–guest systems

	T_2^{FID} (ms)	T_2^{CPMG} (ms)	T_2^{HE} (ms)	T_2^{MAS} (ms)
silicalite-1/methane	0.242	11.7 (56%)	1.02 (50%)	8.8
silicalite-1/ethane	0.203	5.0 (19%)	1.25 (20%)	11.9
silicalite-1/*n*-butane	0.137	6.3 (17%)	0.91 (20%)	6.5
silicalite-1/isobutane	0.176	4.0 (26%)	0.94 (20%)	2.3
silicalite-1/*n*-hexane	0.142	7.5 (32%)	1.24 (45%)	5.5
Na-X/*n*-butane	0.518	10.0 (86%)	1.65 (100%)	14.4

CPMG measurements were performed with a π-pulse distance of $2\tau = 1000\,\mu$s. The percentages in parentheses give the relative echo intensity evaluated by extrapolating the long-time part of attenuation curves to $t = 0$ ms. Two-exponential fitting was used for the Hahn-echo experiment, if the decay was not mono-exponential. Then, the value of T_2^{HE} in the table was obtained from the slowly decaying component.

Now we are only left with the question as to why methane, with tetrahedral symmetry, also shows an anisotropic behavior in slicalite-1, as demonstrated by the relative values of the slowly decaying component of 56% and 50% in Table 1. This can be explained by the intermolecular dipolar interaction between adjacent molecules acting in addition to the intracrystalline interaction. It depends on the symmetry of adsorption sites. Again, the difference in the behavior results from the fact that the adsorption sites in FAU are of cubic symmetry, while they deviate from such a cubic arrangement in silicalite-1.

Fast MAS should quench all broadening effects except the distribution of isotropic values of the chemical shift. For the samples under study, the residual MAS linewidth (expressed in Hz) is not proportional to the applied external magnetic field. Thus, chemical shift distribution does not significantly contribute to the residual line broadening. In addition, there is no drastic increase of the broadening by reducing the rotational frequency from 10 to 3 kHz. Now the question arises, why the residual MAS linewidth for isobutane is about three times larger than for *n*-butane. An explanation can be found by consideration of the concurrence of the narrowing effects. The line narrowing in the MAS NMR spectroscopy of adsorbed molecules is usually based on the fact that dipolar interactions are averaged out by the mobility of the molecule and susceptibility effects by MAS. It is supposed that the isotropic reorientation of the molecules is much faster than the spinning of the sample. If both effects take place in one time interval, phase memory and effect of MAS are disturbed. The self-diffusion coefficients of n-butane in silicalite-1 are more than two orders of magnitude large than those of isobutane [12]. Therefore, the slow mobility of the isobutane molecules leads to a concurrence of molecular mobility and MAS which reduces the MAS narrowing.

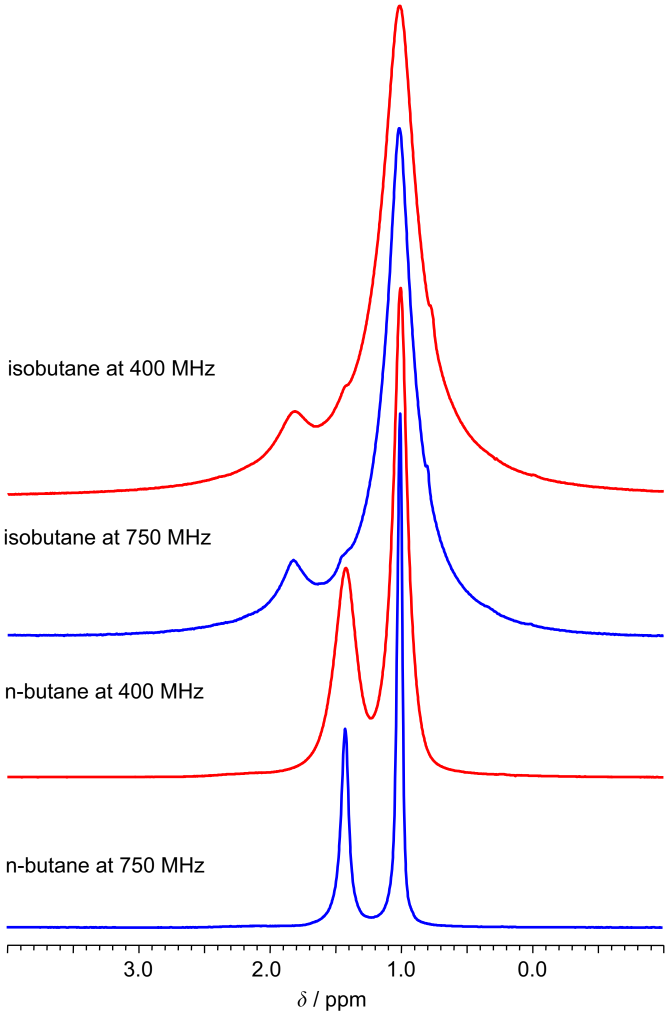

Fig. 4. ^{1}H MAS NMR spectra of *n*-butane and isobutane measured with $\nu_{rot} = 10$ kHz at $\nu_L = 400$ and 750 MHz. Signals at ca. 1, 1.4, and 1.8 ppm correspond to CH_3, CH_2, and CH groups, respectively.

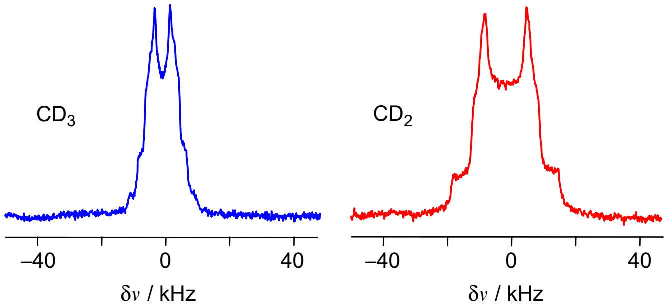

Fig. 5. Static ^{2}H NMR spectra of selectively observed CD_3 and CD_2 groups of fully deuterated *n*-butane adsorbed in MFI-type zeolite obtained at 293 K and 61.4 MHz. Linear regression fits yield quadrupole coupling constants of 11 and 23 kHz and asymmetry parameters $\eta = 0.4$ and 0.24 for CD_3 and CD_2 groups, respectively.

Table 1 shows that MAS is the most effective way for the prolongation of the transverse relaxation, since it gives long relaxation times for the total intensity of the signal. The combination of MAS and PFG has been proven to the very effective in NMR diffusometry of adsorbed molecules [1,11,12].

For the samples under study the usual PFG NMR technique should give correct self-diffusion coefficients, even if, as a result of strong transverse relaxation, only a few percent of the signal can be observed. This has been confirmed for isobutane in silicalite-1 at the temperature of 363 K, where the usual PFG NMR [17] and the MAS PFG NMR [12] experiments result in identical diffusivities.

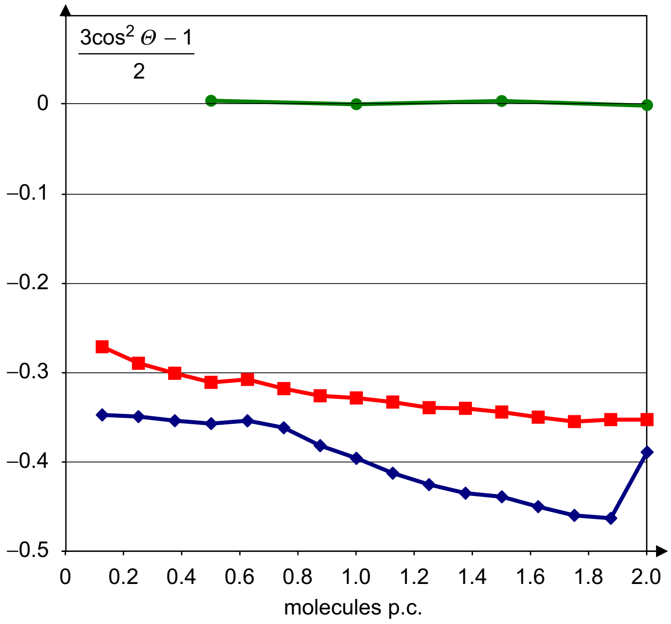

Fig. 6. Order parameter as the function of loaded molecules per cage (FAU type) or per crossing (MFI-type) obtained by snapshots of molecular simulation for 300 K: n-butane in FAU zeolite (●), *n*-butane in MFI zeolite (■) and *n*-hexane in MFI zeolite (◆).

5. Conclusions

The processing of PFG NMR data of the guest molecules in nanoporous host–guest systems, which were obtained from mono-exponential transverse relaxation decay, is uncomplicated. However, any non-exponential decay requires particular care to exclude the possibility that these deviations are caused by spurious amounts of different molecules or by molecules in different states of mobility. A two-component system might dramatically impair the evidence of the PFG NMR experiments with respect to the molecules in the bulk phase of the host–guest system. We have demonstrated that such deviations, however, occur also for a single-component system under special conditions. Deviations from cubic symmetry cause that the dipolar interaction within and between the guests molecules does not average to zero. In this study the phenomenon has been evidenced by several NMR techniques, namely by spin-echo sequences with varying pulse separation, by the CPMG sequence and by MAS NMR and was correlated with the results of molecular simulation. Consequently, PFG NMR diffusion measurements have thus been shown to be applicable even under conditions, where transverse nuclear magnetization deviates from a single-exponential decay. In such cases it is to be concluded that these deviations are in fact caused by the residual influence of the dipolar guest interaction, rather than by the corrupting influence of other compounds or of guest molecules in different states of mobility.

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