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Dynamics of Isobutane inside Zeolite ZSM-5. A Study with Deuterium Solid-State NMR

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Perdeuterated isobutane- d_{10} , when it is adsorbed on zeolite ZSM-5, has been shown to exhibit a superposition of two ^2H NMR Pake-powder patterns with quadrupole constants $C_Q = 2.35$ kHz and asymmetry parameters $\eta = 0.17$ for the CD_3 groups and $C_Q = 23.0$ kHz and $\eta = 0.20$ for the CD group at 153–373 K. The narrowed Pake-powder patterns have been interpreted in terms of the motional behavior of isobutane molecules located at the channel intersections of the zeolite framework. The dynamic behavior of isobutane is complex and includes probably both fast intramolecular rotations and large amplitude hops of the molecule as a whole. For example, the motion of the CD group may be effectively described as consisting of the combination of the precession of the CD group around some axis Z, which makes up the angle $\gamma \approx 47^\circ$ with the direction of the C–D bond, and fast hops of the axis Z itself between four nonequally populated orientations, determined by the geometry of the zeolite channel segments. Simultaneously, fast rotation of the methyl groups occurs around two different C_3 axes. The activation energies and rotational correlation times at 373 K have been estimated to be 13.5 kJ/mol and 41 ps for the methyl groups and 17.7 kJ/mol and 1200 ps for the methene group, respectively.

Introduction

The practical importance of zeolite ZSM-5 for catalysis¹ and separation² of hydrocarbons stimulated studies of the dynamics of alkanes in this zeolite with both experimental and theoretical methods. Pulse-field gradient NMR and quasi-elastic neutron scattering (QENS)^{3,4} provide information about diffusion coefficients (up to C_{16} -alkane in zeolite ZSM-5), whereas molecular dynamics simulations were used to gain a great deal of understanding about alkanes distribution in the zeolite pores and the mechanism of diffusion.^{5–7} However, theoretical simulations provide us with some idealized view on the mechanism of diffusion, because they do not take into account the motional behavior of separate fragments of the alkane hydrocarbon chain during its translational diffusion in the zeolite channel system.

Diffusivity of isobutane in ZSM-5 has been measured recently with QENS.⁸ It was demonstrated that the diffusion coefficient for the branched alkane, isobutane, is 3 orders of magnitude lower than that for the linear n -butane.⁹ Isobutane was concluded to be localized at channel intersections of ZSM-5 and to move in the zeolite by means of jumps from one channel intersection void to another one.⁸ However, the dynamics of the molecule at channel intersections was not accessible on the time scale of the experiment.

Deuterium solid-state NMR (^2H NMR) has been shown to be a powerful technique to probe the dynamics of organic molecules adsorbed in zeolites pores.^{10–18} The line shape for ^2H NMR, being completely defined by intramolecular quadrupole

interaction,^{19–21} is especially sensitive to the mode of molecular motion and its rate.^{19,20} Therefore, by analyzing ^2H NMR line shapes, as well as relaxation rates, one can evaluate the nature of the molecular motion and its rate.

In this paper, a description is given of ^2H NMR line shapes for isobutane- d_{10} and isobutane- $[2d_1]$ adsorbed on zeolite ZSM-5. Interpretation of the separate line shapes from methyl and methene groups contributing to the total ^2H NMR spectrum of the adsorbed alkane is made in terms of different mobility exhibited by the different CD_n ($n = 1$ or 3) groups of the adsorbed alkane.

Experimental Section

Materials. A H-ZSM-5 sample with a Si/Al ratio of 58 was prepared from Na-ZSM-5 via NH_4^+ ion exchange and subsequent calcination at 820 K as described in ref 22. The obtained zeolite sample was characterized by X-ray powder diffraction and chemical analyses. Deuterated alkanes, isobutane- d_{10} with 98% of ^2H isotope enrichment, and isobutane- $[2d_1]$ with 82% of ^2H isotope enrichment were used in this work.

Sample Preparation. To prepare samples for the NMR experiments, approximately 0.3 g of zeolite was loaded in a 5 mm (o.d.) glass tube connected to a vacuum system. The sample was then heated at 720 K for 1.5 h in air and for 4 h under vacuum to a final pressure above the sample of 10^{-5} Torr (1 Torr = 133.3 Pa). After cooling the sample back to room temperature, the zeolite was loaded with about two isobutane molecules per unit cell. A total of 16 Torr of isobutane was frozen with liquid nitrogen on the zeolite sample from a calibrated volume (140 mL) in several adsorption steps to reach the required amount of two molecules per unit cell (uc). After adsorption, the neck of the tube was sealed off, while the zeolite

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sample was maintained in liquid nitrogen to prevent its heating by the flame. Then, the sample was kept at 373 K for 12 h to allow the alkane to be evenly redistributed inside the zeolite void. The sealed sample was then transferred into an NMR probe for recording the ^2H NMR spectra.

NMR Measurements. ^2H NMR experiments were performed at 61.424 MHz on a Bruker MSL-400 spectrometer using a high-power probe with a 5 mm horizontal solenoid coil. All ^2H NMR spectra were obtained by Fourier transformation of the quadrature-detected phase-cycled quadrupole echo arising in a pulse sequence²³

$$\left(\frac{\pi}{2}\right)_{\pm X} - \tau_1 - \left(\frac{\pi}{2}\right)_Y - \tau_2 - \text{acquisition} - t \quad (\text{i})$$

where $\tau_1 = 30 \mu\text{s}$, $\tau_2 = 34 \mu\text{s}$, and t is a repetition time for the sequence i during the accumulation of the NMR signal. The duration of the $\pi/2$ pulses was $5.0 \mu\text{s}$. Spectra were typically obtained with 500–5000 scans and a repetition time $t = 0.4$ – 2 s. Inversion–recovery experiments to derive spin–lattice relaxation times (T_1) were carried out using the pulse sequence²⁴

$$(\pi)_X - t_v - \left(\frac{\pi}{2}\right)_{\pm X} - \tau_1 - \left(\frac{\pi}{2}\right)_Y - \tau_2 - \text{acquisition} - t \quad (\text{ii})$$

where t_v was a variable delay between the 180° $(\pi)_X$ inverting pulse (as in standard inversion–recovery pulse sequence²⁴) and the quadrupole echo sequence i.

The temperature of the samples was controlled with a variable-temperature unit BVT-1000 with a precision of ± 1 K. The samples were allowed to equilibrate at least 15 min at a given temperature before the NMR signal was acquired. Line shapes were fitted to theoretical powder patterns using a nonlinear, least-squares tensor-fitting routine.

Theoretical Background

^2H NMR spectra from polycrystalline organic solids are known to be dominated by quadrupole coupling.^{19–21,25,26} This coupling is of intramolecular origin^{19–21} and strongly affected by the mode and the rate of the molecular motion in which a molecule is involved.^{20,25–27}

For molecules rigid on the ^2H NMR time scale, τ_{NMR} (i.e., when correlation times τ_C for molecular reorientation and internal motions satisfy the condition $\tau_C \gg \tau_{\text{NMR}} \approx Q_0^{-1} \approx 5 \times 10^{-6}$ s, where $Q_0 = C_Q = e^2qQ/h$ is the quadrupole coupling constant unaffected by any motional averaging),²⁸ ^2H NMR spectra represent Pake-type powder patterns.^{20,21} The dominant features of these line shapes are two strong peaks separated by the splitting $(3/2)Q_0$ and two shoulders separated by $(3/4)Q_0$ [see Figure 1A]. For deuterium bonded to tetrahedral carbon atoms in polycrystalline organic solids, $(3/4)Q_0$ is usually 120–130 kHz and the asymmetry parameter η is close to zero.^{25,27,29,30} If a CD_3 group of an organic molecule undergoes fast threefold jumps or diffusional rotation about the C– CD_3 bond with a correlation time $\tau_R \ll \tau_{\text{NMR}}$, that is, $\tau_R < 10^{-7}$ – 10^{-6} s, and if isotropic reorientation of the molecule as a whole is slow ($\tau_C \gg \tau_{\text{NMR}}$), then the line shape of the spectrum for CD_3 groups will be similar to that of rigid molecules, but with the quadrupole splitting reduced to the value of $(3/4)Q_1$ (Figure 1B),^{27,29,30} according to the relation

$$Q_1 = Q_0 \frac{3 \cos^2 \alpha - 1}{2} \quad (1)$$

Here, α is the rotation angle between the C–D and C– CD_3

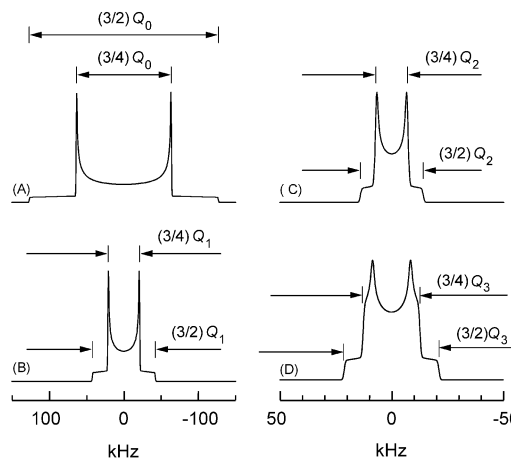


Figure 1. Theoretical ^2H NMR spectra: (A) polycrystalline sample (static CD_3 group, $C_Q = e^2qQ/h = Q_0 = 169.5$ kHz, $\eta = 0$); (B) rapid rotation of the CD_3 group about one C_3 axis, angle $\alpha = 109.47^\circ$, $Q_1 = (1/3)Q_0$; (C) rapid rotation of the CD_3 group about two axes, angles $\alpha = 109.47^\circ$, $\beta = 109.47^\circ$, $Q_2 = (1/9)Q_0$; (D) rapid hops by the angle $\Theta = 86^\circ$ between two equally populated sites of CD_3 group rapidly rotating about C_3 axis, $Q_3 = (1/6)Q_0$, $\eta = 0.2$. An individual line shape function of the form $g(x) = 1/(\sigma\sqrt{2\pi}) \exp(-x^2/(2\sigma^2))$ with $\sigma = 0.5$ kHz was used in all simulations.

bonds. For the ideal tetrahedral geometry of the C– CD_3 fragment, $\alpha = 109.47^\circ$ and $Q_1 = (1/3)Q_0$. In practice, typical values of the reduced splitting, $(1/3)Q_0$, are 35–40 kHz.^{27,30,31}

If a CD_3 group is involved in an additional rotation (either three or higher fold jumps) about a second axis tilted by the angle β with respect to the first axis, then, again, its ^2H NMR spectrum has a quadrupole splitting reduced to $(3/4)Q_2$ ³² (Figure 1C) with an effective quadrupole constant equal to

$$Q_2 = Q_0 \left(\frac{3 \cos^2 \alpha - 1}{2} \right) \left(\frac{3 \cos^2 \beta - 1}{2} \right) \quad (2)$$

If β is equal to $\alpha \approx 109.47^\circ$, then $Q_2 = (1/9)Q_0$ and the splitting is typically of $(3/4)Q_2 \approx 12$ – 14 kHz. Similarly, in the case of the existence of a third rotation (jump) axis, tilted by the angle γ with respect to the second rotation axis, there will be a further reduction of the quadrupole splitting up to $(3/4)Q_3$, where

$$Q_3 = Q_0 \left(\frac{3 \cos^2 \alpha - 1}{2} \right) \left(\frac{3 \cos^2 \beta - 1}{2} \right) \left(\frac{3 \cos^2 \gamma - 1}{2} \right) \quad (3)$$

Thus, for tetrahedral angles $\alpha = \beta = \gamma = 109.47^\circ$, the finally observed splitting is $(3/4)Q_2 = (1/36)Q_0$.

If a CD_3 group rapidly rotating around the C– CD_3 bond group exhibits also fast large-angle hops between two or more sites in nontetrahedrally arranged positions, with or without being equivalent, the quadrupole splitting reduces further and anisotropy appears in the spectrum³³ (Figure 1D). For example, in the case of a fast exchange of the direction of the C– CD_3 group between two sites with an angle Θ between the directions of the C–C bond in each position, the dependences of the asymmetry parameter η and quadrupole constant vs the angle Θ are defined by the following expressions:³³

$$\frac{C_Q}{C_{Q_0}} = \frac{1}{2} \quad \text{and} \quad \eta = 3|\cos \Theta| \quad \text{at} \quad |\cos \Theta| \leq \frac{1}{3}$$

$$\frac{C_Q}{C_{Q_0}} = \frac{1}{4}(1 + 3|\cos \Theta|) \quad \text{and} \quad \eta = 3\frac{1 - |\cos \Theta|}{1 + 3|\cos \Theta|} \quad \text{at} \quad \frac{1}{3} \leq |\cos \Theta| \leq 1 \quad (4)$$

Here, C_Q is an effective value of the quadrupole constant in the presence of exchange and C_{Q_0} is the quadrupole constant in the absence of exchange.

When the correlation time τ_C for the isotropic reorientation (rotation) of the molecule as a whole becomes comparable to τ_{NMR} , a broadening of the spectrum is observed and the sharp features disappear.²⁸ For rapid isotropic reorientation, as in liquids, when $\tau_C \ll \tau_{\text{NMR}}$, the quadrupole splitting is averaged to zero and a single line with a Lorentzian shape is observed at ω_1 , the Larmor frequency of the deuterium nucleus.¹⁹

Although ^2H NMR line shape provides information about the type of motion for a CD_3 group in a molecule, it contains no further information about the rates of this process. For a number of experimental situations, this information may be obtained from the special measurements of nuclear relaxation rates, $1/T_1$. Spin–lattice relaxation time, T_1 , is given by the following expression for isotropically reorienting molecules exhibiting Lorentzian NMR line shape¹⁹

$$\frac{1}{T_1} = \frac{3}{40} \left(1 + \frac{\eta^2}{3}\right) (2\pi C_Q)^2 \left(\frac{\tau_C}{1 + \omega_1^2 \tau_C^2} + \frac{4\tau_C}{1 + 4\omega_1^2 \tau_C^2} \right) \quad (5)$$

where τ_C is a rotational correlation time for isotropically reorienting molecule.

For an anisotropically reorienting methyl group in a static solid (threefold jumps and continuous diffusion of a CD_3 group about a C_3 symmetry axis), explicit expressions were developed by Torchia and Szabo.³³ For example, for the threefold jump model of the methyl group reorientation, the following expression for T_1 is valid:³⁴

$$\frac{1}{T_1} = \frac{1}{8} \left(\frac{3}{2} \pi C_Q \right)^2 \left\{ \frac{\tau_R}{1 + \omega_1^2 \tau_R^2} \left[\sin^2 2\alpha (\cos^2 \theta + \cos^2 2\theta) + \sin^4 \alpha \left(\sin^2 \theta + \frac{1}{4} \sin^2 2\theta \right) - 8 \sin^3 \alpha \cos \alpha (\sin^3 \theta \cos \theta) \cos 3\Phi \right] + \frac{\tau_R}{1 + 4\omega_1^2 \tau_R^2} \left[4 \sin^2 2\alpha (\sin^2 \theta + \frac{1}{4} \sin^2 2\theta) + \sin^4 \alpha (1 + 6 \cos^2 \theta + \cos^4 \theta) + 8 \sin^3 \alpha \cos \alpha (\sin^3 \theta \cos \theta) \cos 3\Phi \right] \right\} \quad (6)$$

where τ_R is the correlation time of the threefold rotational jumps, θ and Φ are the polar angles describing the orientation of the rotation axis for the CD_3 group with respect to the external magnetic field \mathbf{B}_0 , and α is the angle between the rotation axis and the main axis of axial electric field gradient tensor (the directions of the C–D bond). $\theta = 90^\circ$ at the perpendicular edges of the powder pattern, whereas $\alpha \approx 109.47^\circ$ for the methyl group.

Results and Discussion

Figure 2 shows the ^2H NMR spectrum for isobutane- d_{10} adsorbed on H–ZSM-5. Within the temperature range 153–

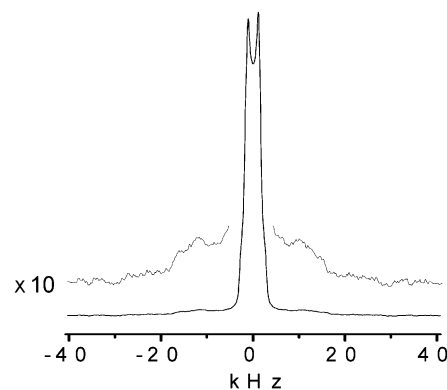


Figure 2. ^2H NMR spectrum at 373 K of isobutane- d_{10} adsorbed on H–ZSM-5 with the loading of two molecules per uc.

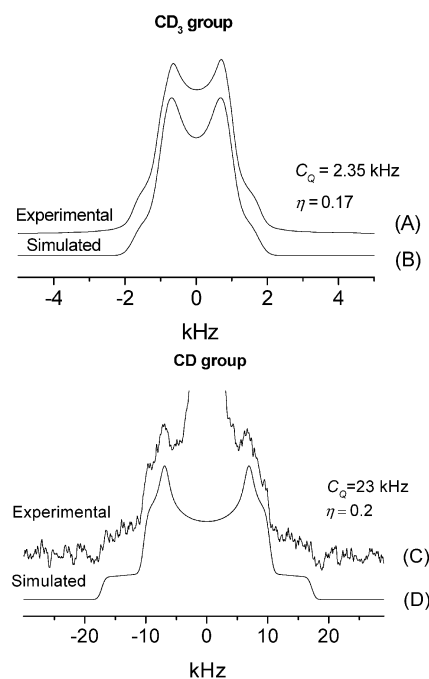


Figure 3. Simulation of the experimental ^2H NMR line shapes for CD_3 and CD groups of isobutane- d_{10} in H–ZSM-5: (A) experimental spectrum for CD_3 groups; (B) a fit to the line shape of the CD_3 – groups with $C_Q = 2.35$ kHz and $\eta = 0.17$; (C) experimental spectrum for the CD group; (D) a fit to the line shape of the CD – group with $C_Q = 23.0$ kHz and $\eta = 0.20$.

373 K, the spectrum represents a superposition of two Pake-powder patterns with quadrupole splittings, $(3/4)Q_0$, of about 1.8 and 17 kHz. These two experimental line shapes are fitted theoretically with quadrupole constants $C_Q = 2.35$ and $C_Q = 23$ kHz and asymmetry parameters $\eta = 0.17$ and $\eta = 0.2$ for the intense and weak signals, respectively (Figure 3). According to the expected integral intensity ratio 9:1 for the CD_3 and CD groups in the molecule, the intense and narrow signal with $C_Q = 2.35$ kHz is attributed to the methyl groups, whereas a weak and broad signal with $C_Q = 23$ kHz is assigned to the CD deuterons. The observed quadrupole constants for both CD_3 and CD groups are essentially reduced compared to the “rigid” CD_3 or CD_2 groups of alkanes, which are usually about 170 kHz.^{27–30} Observation of the Pake-powder patterns for the adsorbed isobutane implies that both the CD_3 and CD groups of the alkane molecule are involved in some fast anisotropic motion and there is no isotropic reorientation of the adsorbed isobutane faster than the reciprocal value of the observed quadrupole constants, that is, $\tau_C \gg Q_0^{-1} \approx 4 \times 10^{-4}$ s. We conclude that the observed

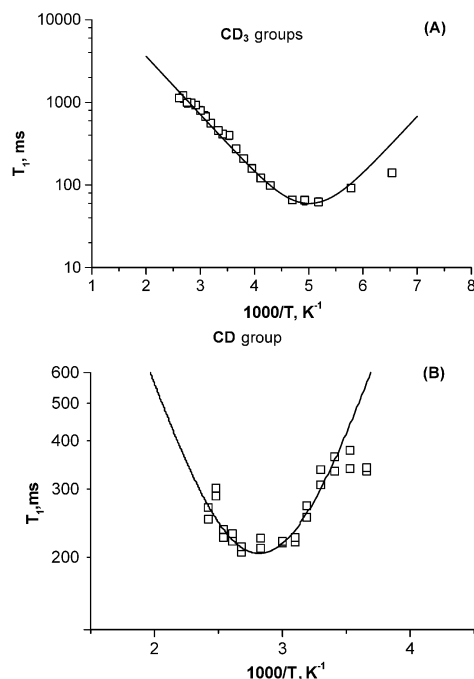


Figure 4. ^2H NMR spin–lattice relaxation data at the perpendicular edges of the powder patterns of CD_3 groups (A) and CD group (B) for isobutane adsorbed on H–ZSM-5 at the loading of two molecules per uc. T_1 for CD_3 was measured in isobutane- d_{10} , and T_1 for CD was measured in isobutane- $[2d_1]$. The solid line for CD_3 group is a fit by the theoretical expression 6 for perpendicular edges of the powder pattern with $\alpha = 109.47^\circ$ and the following effective parameters: quadrupole constant $C_Q = 43$ kHz; preexponential factor $\tau_0 = 0.5$ ps; activation energy $E_a = 13.5$ kJ/mol. Contribution to spin–lattice relaxation time at perpendicular edges of powder pattern is the weighted average of T_1 of the two contributing orientations with $\theta = 90^\circ$ and $\theta = 35.26^\circ$.³⁴ The relative weights of these orientations are 0.625 and 0.375, respectively. Φ was averaged over all possible orientations. The solid line for CD is a fit by the expression 5 with the following effective parameters: $C_Q = 21$ kHz; $\tau_0 = 3.95$ ps; $E_a = 17.7$ kJ/mol.

NMR line shapes should be related to the fast anisotropic rotations of both CD_3 and CD groups of the molecule.

Spin–lattice relaxation times T_1 were measured as a function of temperature at 153–373 K for deuterons of both CD and CD_3 groups of the adsorbed alkane (see experimental points in Figure 4). The variation of the logarithm of T_1 as a function of the reciprocal temperature ($1/T$) is linear through the temperature range 233–373 K for the CD_3 groups (Figure 4). In this temperature range, the spin–lattice relaxation of the CD_3 is defined by fast internal motions with characteristic times τ_C satisfying the condition $\omega_1\tau_C \ll 1$, that is, $\tau_C \ll 2.6 \times 10^{-9}$ s. At 373 K, the experimental value of the spin–lattice relaxation times T_1 for the CD_3 group is 1.06 s. Using eq 5 (with $\eta = 0$ and $Q_0 \approx 170$ kHz) as a rough approximation for $1/T_1$ and taking into account that only the rapidly fluctuating component of the quadrupole coupling tensor is responsible for the spin–lattice relaxation, we may estimate that a fast internal motion with $\tau_C \geq 0.5 \times 10^{-11}$ s is responsible for the spin–lattice relaxation of the CD_3 deuterons. The estimated value of τ_C is in a good agreement with typical values of correlation times for diffusional rotations (jumps) about C–C bonds in hydrocarbons.^{13,17,18,35} The activation energy of 13.5 kJ/mol estimated for the reorientation of the CD_3 groups from the slope of $\ln T_1$ is also in good accordance with those determined for torsional vibrations in ethane³⁶ or predicted for transformations between trans and gauche conformations in other alkanes.⁶

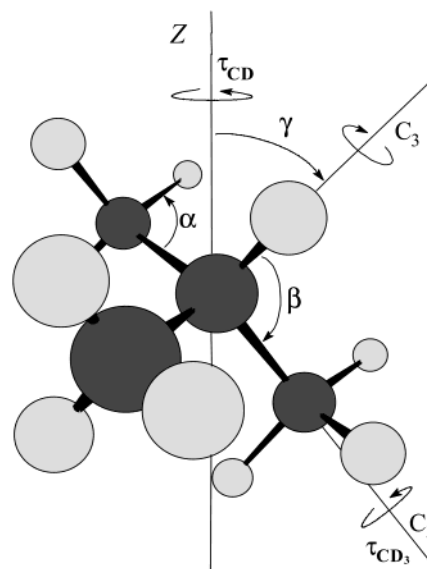


Figure 5. Possible motions for the methyl (CD_3) and methene (CD) groups of the adsorbed isobutane molecule located in a channel intersection site of zeolite ZSM-5 before the precession axis Z is involved in fast large-amplitude hops among four orientations determined by the geometry of the channel segments.

It should be noted that T_1 minima for CD_3 and CD groups, where $\omega_1\tau_C \approx 1$, are separated from each other by 200 K (353 and 183 K). This allows us to estimate (at E_a for molecular reorientation in the zeolite pores ≈ 13 kJ/mol, vide supra) that the rate of the motion of CD_3 groups differs at least by 1 order of magnitude from that of the CD group at the same temperature, the motion of the methyl groups being faster. It is reasonable to suggest that fast rotation around the CD_3 –CD bond is responsible for the relaxation of the methyl group, whereas the reorientation of the molecule as a whole should be responsible for the relaxation of the CD group because it is rigidly bound to the molecule and there is no intramolecular motion for the CD group compared to that for methyl groups. Therefore, the experimental T_1 data for CD_3 were fitted with the expression 6 of Szabo and Torchia,³⁴ and T_1 data for the CD were roughly approximated with the T_1 expression for isotropically reorienting molecules¹⁹ (eq 5) (Figure 5).

The activation energy for the reorientation of the CD_3 groups derived from the fit ($E_a = 13.5$ kJ/mol) is in good agreement with the value estimated (vide supra) from the linear part of the experimental dependence of the logarithm of T_1 vs $1/T$. The activation energy estimated for the motion of the CD group, which reflects the reorientation of the molecule as a whole, is 17.7 kJ/mol. To the best of our knowledge, it is higher than E_a for the intramolecular rotation of either methyl or methylene groups (or trans–gauche interconversion) in alkanes.⁶ The characteristic times of the reorientation of the CD_3 and CD groups, derived from the theoretical fits are $\tau_{\text{CD}_3} = 41$ ps and $\tau_{\text{CD}} = 1200$ ps at 373 K. These data indicate that the rates of the reorientation of the CD_3 and CD groups differ by 2 orders of magnitude, the motion of the methyl groups being notably faster.

Reorientational correlation time τ_C for the CD_3 , which is in good agreement with the reorientational correlation time for rotations of the methyl (or methylene) group in alkanes,^{13,17,18,35} corresponds evidently to internal rotation of the methyl groups, whereas τ_C for the CD reflects the reorientation of the molecule as a whole. It may correspond either to translational motion of the alkane molecule over the ZSM-5 zeolite framework³⁷ or to

a local motion in the channel intersections. The results of the quasi-elastic neutron scattering study of isobutane diffusivity in ZSM-5⁸ imply that the residence time of the isobutane molecule at a channel intersection site is $\sim 10^{-6}$ – 10^{-7} s at 300–373 K. This profound difference in time between successive jumps among adsorption sites and τ_C for the CD allows us to assume that the observed NMR line shapes (narrowed powder patterns, compared to rigid CD₃ group) for the CD_n ($n = 1, 3$) groups should be interpreted in terms of anisotropic rotational motion of isobutane located at a channel intersection site. Therefore, we further interpret the observed line shapes (quadrupole constants C_Q and asymmetry parameters) in terms of motional behavior of the CD₃ and CD groups of isobutane inside the void of the channel intersection.

Fast rotation of the methyl groups should result in the reduction of the quadrupole constant C_Q expected for the rigid CD₃ group by 3 times (see formula 1), that is, the expected value of $(3/4)Q_1$ would be ~ 42.5 kHz. Because the observed C_Q is equal to 2.35 kHz, one can reasonably assume that further reduction of the quadrupole splitting can arise from additional anisotropic rotational motion of the methyl groups. It is reasonable to assume that the entire (CD₃)C fragment effectively rotates also about its threefold C_3 axis, that is, around the C–D bond of the methene group, as is observed in the tertiary butyl group of solid and adsorbed in ZSM-5 *tert*-butyl alcohol¹⁶ or in solid *tert*-butyl halides.³⁸ This effective rotation of the methyl group around a second C_3 axis with an angle $\beta = 109.47^\circ$ would result in a further reduction of C_Q by a factor 3. However, the expected total decrease of unaveraged C_Q by a factor 9 does not fit with the experimentally observed quadrupole constant $C_Q = 2.35$ kHz. Further reduction of the quadrupole constant may occur if we assume that there exists some additional anisotropic axial movement (rotation or libration) of the molecule as a whole. For the qualitative estimation, it may be considered as the rotation corresponding to a precession of the C_3 axis, passing through the C–D bond of the methene group, around some axis Z . The angle γ between the rapidly rotating (CD₃)₃C– fragment and the precession axis Z (third axis for rotation of the methyl groups) estimated from the eq 3 should be 49.8° . Note that fast rotation of the (CD₃)₃C– fragment about the C_3 axis makes all three methyl groups equivalent and therefore, additional precession of this fragment inclined by the angle γ with respect to the precession axis Z provides no different signals from the methyl groups.

For this model of rotational motion of the methyl group around three axes, the motion of the C–D group should correspond to a precession of the C–D vector of the methene group around the same precession axis Z . The angle between the direction of the C–D bond and the precession axis Z found from the experimentally observed quadrupole constant $C_Q = 23$ kHz based on eq 1 is 49.4° . Thus, the very close values of the angles for the precession of the C–D bond around some axis Z and the angle γ for the rotation of the CD₃ around the third axis allow us to conclude that there is in fact an *effective* rotational motion (precession) of the isobutane molecule around some axis Z , which makes up the angle γ of about 49° with the direction of the C–D bond of the CD group. The model of this motion is represented in Figure 5.

It should be noted that we have not yet taken into account so far the observed nonzero asymmetry parameters of ²H NMR spectra in the interpretation of the reduced quadrupole constants. Indeed, the motion of both CD₃ and CD groups is more complex than their rotations and precession around the selected axis Z . The observed value of the asymmetry parameter $\eta \approx 0.2$ is

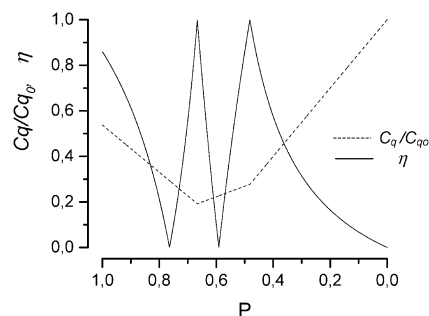


Figure 6. Predicted dependences of the effective values for η (solid line) and C_Q (dashed line) vs the probability, P , of C–D bond orientation toward the straight channel for the case of the fast large-amplitude hops of the C–D bond among four possible orientations defined by the geometry of the channel segments of zeolite ZSM-5. To derive this dependence, the angles between segments of neighbor straight channels was taken as 180° and between zigzag channels it was assumed to be 112° .³⁷

indicative of this fact. Because the value of the asymmetry parameter η for powder pattern of the static deuterium nuclei in the CD_n groups is usually equal to zero, $\eta \approx 0$, it is reasonable to assume that the nonzero asymmetry parameter, that is, $\eta \approx 0.2$, for the adsorbed isobutane-*d*₁₀ results from the some additional motion of the isobutane molecule localized at the channel intersection. This motion may consist of large-angle reorientations of the molecule as a whole between two or more sites in noncubic/nontetrahedrally arranged positions of the molecule inside the channel intersection void.

According to the theoretical transition path sampling calculation by Vlucht et al.,³⁹ the isobutane molecule, located at a channel intersection site with a residence time of $\sim 10^{-7}$ s, performs infrequent (compared to residence time) hops to the other intersection site via either straight or zigzag channel. The direction of the C–H bond in the methene group of the alkane is oriented perpendicular to the axis of the channel in the transition state before the hop. Therefore, we can assume that the molecule at a channel intersection can also perform large angle hops among four orientations, which the molecule can occupy before the hop to the other intersection site. These orientations are determined by the geometry of the channel segments, the direction of the C–H bond of the methene group in each of the orientations being perpendicular to the channel axis.

Figure 6 shows the theoretical dependence of the effective values for η and C_Q vs the probability, P , of the orientation of the C–D bond of the methene group toward the direction of a zigzag channel in the case of rapid exchange among four orientations of this C–D bond determined by the geometry of the ZSM-5 channel segments. It is seen that five possible probabilities P can fit the experimentally determined asymmetry parameter $\eta \approx 0.2$. Theoretical estimations of the hopping rates for the straight and zigzag channels by Vlucht et al.³⁹ indicate that the rate of the molecule hopping for the straight channels is higher by at least 3 times compared to that for zigzag channels. This means that the probability of orientation of the C–D bond toward a straight channel before the hop to the other intersection site should always exceed 70%. In this case, the experimental value $\eta \approx 0.2$ corresponds to 77% of probability of C–D bond orientation toward a straight channel.

Thus, the asymmetry parameters in the powder patterns of the adsorbed isobutane-*d*₁₀ can be interpreted in terms of the hops of the precession axis Z among four orientations determined by the geometry of the zeolite channel segments. Each orientation of the axis Z seems to be perpendicular to the axis

of the channel³⁹ toward which the molecule can jump to reach the neighbor intersection site.

It follows from the Figure 6 that $C_Q/C_{Q_0} = 0.66$ for $\eta \approx 0.2$ and 77% of probability of C–D bond orientation toward the straight channel in a model of four sites reorientation of the precession axis Z. Within the frame of this model, the experimental values of $C_Q = 2.35$ and 23 kHz for CD_3 and CD groups correspond to $C_{Q_0} = 3.35$ and 35 kHz (before CD_n are involved in the exchange among four orientations of the axis Z). From the C_{Q_0} values for the methyl and methene groups, we derive two sets of the angle between the precession axis Z and the direction of the C–D bond in the methene group of the isobutane molecule. We obtain $\gamma = 46.7^\circ$ from $C_{Q_0}(CD)$ and $\gamma = 47.8^\circ$ from $C_{Q_0}(CD_3)$. These last γ values represent more precise values with respect to the estimates of γ calculated without taking into account the hops of the precession axis among four orientations at a channel intersection site. From these data, we conclude that the C–D bond precesses around the axis Z tilted by the angle $\gamma \approx 47^\circ$ with respect to the axis Z and simultaneously the Z axis itself hops among four orientations. It is not possible to define the exact orientation of the precession axis Z with respect to the direction of the channel axes for the molecule residing in a channel intersection from the experimental data; we could only assume that its direction is perpendicular to the channel axis that may correspond to the transition state for the jump to the neighbor intersection site.³⁹

The reasons for this specific mode of the isobutane motion at a channel intersection are not clear to date and cannot be rationalized unequivocally. It does not seem to be related to the influence of Brønsted acid sites located at channel intersection sites of the zeolite because isobutane-*d*₁₀ adsorbed on pure silicalite and sodium-form ZSM-5 exhibits similar spectral parameters (C_Q and η) in the ²H NMR spectrum.⁴⁰ Any chemical reactions cannot affect the observed line shape or the motional behavior of the adsorbed alkane either, because there is no chemical transformation of isobutane on ZSM-5 at 300–373 K (e.g., see ref 41).

The diameter of the channel intersection is about 8 Å,³⁷ whereas the kinetic diameter of the isobutane molecule is about 5.5 Å.⁴² So, the molecule is smaller, and therefore, one could have expected free isotropic rotation for a molecule located in a channel intersection with a Lorentzian ²H NMR line shape for the adsorbed isobutane. However, the channel intersection void is not spherical. Therefore, one can assume that the specific influence of the walls of the nonspherical intersection void provides the observed specific anisotropic mode of motion of the adsorbed isobutane by its collisions with the zeolite walls.

It should be realized that this model of isobutane local mobility in the ZSM-5 framework represents only a rationalization of the experimental NMR data. It is obvious that, because of the complexity of the zeolite framework system, the local mobility of isobutane may be more complex than a simple superposition of several well-defined independent movements. Nevertheless, our model reasonably describes the observed ²H quadrupole parameters; therefore, one may expect that it also reproduces some certain peculiarities of isobutane local motions in the zeolite, such as large-scale librations (hops) and internal rotations. We hope that peculiarities of isobutane motional behavior inside ZSM-5 may be deeper clarified in the future by combining the experimental NMR and theoretical molecular dynamics techniques.

Conclusion

From the analysis of both the ²H NMR line shape and spin–lattice relaxation time of isobutane adsorbed on zeolite ZSM-

5, the following conclusions can be drawn about the spectral features and the motional behavior of isobutane inside the zeolite channel system. Perdeuterated isobutane-*d*₁₀ exhibits a superposition of two ²H NMR Pake-powder patterns with quadrupole constant $C_Q = 2.35$ kHz and asymmetry parameter $\eta = 0.17$ for the CD_3 groups and $C_Q = 23.0$ kHz and $\eta = 0.20$ for the CD group at 153–373 K. The narrowed Pake-powder patterns are assigned to motions of the isobutane molecule located at a channel intersection site of the zeolite. The motion of the CD group may be effectively described as consisting of the combination of the precession of the C–D group around some axis Z, which makes up the angle $\gamma \approx 47^\circ$ with the direction of the C–D bond, and additional effective hops of the axis Z itself among four nonequally populated orientations defined by the geometry of the channel segments outward from the channel intersection. Simultaneously, fast rotation of the methyl groups occurs about two different C_3 axes. The activation energies and rotational correlation times at 373 K for the methyl groups are 13.5 kJ/mol and $\tau_{CD_3} = 41$ ps. For methene group, they are 17.7 kJ/mol and $\tau_{CD} = 1200$ ps, respectively. The proposed model for the local reorientation of isobutane in the void of the channel intersections, as the rationalization of NMR data, reflects some important peculiarities of isobutane dynamics in the zeolite framework, which may be deeper clarified in the future by combining the experimental NMR and theoretical molecular dynamics techniques.

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