Proton Transfer in Hydrated Microporous Aluminosilicates: A ^{1}H NMR Study of Zeolite Chabazite

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A NMR approach to in situ precise determination of the proton exchange rate in water molecules sorbed on microporous crystals is presented and applied to hydrated zeolite chabazite and its various ion-substituted forms. This approach has allowed us to measure a frequency of proton exchange in the range from 2×10^1 to 2×10^3 s^{-1}. The observed exchange is interpreted as a result of the proton-transfer reaction between H_2O molecules and chemical defects represented by Brønsted acidic sites. For the substances studied, the barrier for this reaction is found to vary in the range 45−60 kJ/mol.

Introduction

The proton transfer in the cages of microporous aluminosilicates, zeolites, plays an important role in determining properties of these substances as catalysts and ion conductors.[1,2] In recent years, mechanisms of the proton-transfer reactions in zeolites have been extensively examined using NMR[3−7] and infrared spectroscopy[8−11] as well as ab initio quantum chemistry calculations.[11−14] Much attention has been focused on reactions of proton transfer between various hydrocarbon molecules and active sites in protonated zeolites. In some cases, reliable data on the rates of these reactions have been gained from observations of H/D exchange between zeolite and sorbate.[6,11] However, for the water molecules—the most usual sorbate in zeolites—there are only theoretical estimations of the energetical characteristics of these reactions,[12−14] whereas most of experimental data are of qualitative character.[8,9,15]

In this work we present the results of a NMR study of the rates of proton transfer in hydrated zeolite chabazite and its cation-exchanged forms. According to the previous studies this zeolite displays a rather high proton conductivity.[2] The catalytic activity of chabazite has been investigated in some other works.[16,17]

In the chabazite structure, water molecules occupy different structural positions in channels coordinating partially with extraframework cations.[18] At ambient conditions and at elevated temperatures H_2O molecules jump between their positions with characteristic frequency exceeding 10^6 s^{-1}.[19] A fast diffusive mobility of the molecules permits to develop an interesting NMR approach to in situ precise determination of the frequency of the intermolecular proton exchange in the zeolite channels.

Experimental Section

Materials. A natural Ca-chabazite (Hilok river, Transbaikalia, Russia) with the composition $(Ca_{1.7}Na_{0.2}K_{0.1})[Al_{3.7}Si_{8.3}O_{24}] \cdot 12.7H_2O$ was used in this work. From X-ray data its unit cell was determined to be pseudohexagonal (space group $R\bar{3}m$) with

$a = 13.771(4)$ and $c = 14.988(5)$ Å. Colorless transparent single crystals (average size 2−5 mm) and powdered samples with particles of ≤ 50 μm were used for NMR experiments.

Powder samples of cation-substituted (Na, K, Ba) chabazites with the degree of substitution more than 90% were obtained by ion exchange in 1 N aqueous chloride solutions (400 K, 1 week, one renewal of the exchanged solution). Li-chabazite was obtained by ion exchange in $LiNO_3$ melt (550 K, 1 week) with subsequent removing residual salt in water at 420 K (24 h). In equilibrium with air of $\approx$70% relative humidity at 290 K the number of water molecules per unit sell was determined to be 9.0, 9.5, 10.5, and 11.5 for Li-, K-, Ba-, and Na-chabazite, respectively.

A few samples were prepared by treating the initial zeolite with a dilute HCl solution (pH = 4) at 290 K for different exposition times. As described in the literature,[20] a similar procedure can result in a weak H substitution in zeolite without dealumination.

NMR Measurements. This work is based mainly on the ^{1}H NMR broad-line spectra resulting from the magnetic dipole−dipole interaction of protons. For the Na-exchanged sample, the ^{23}Na NMR spectra (the $-^1/_2 \leftrightarrow {}^1/_2$ transition) affected by the second-order quadrupole interactions of the nuclear quadrupole moment with electric field gradients were also registered. All spectra were recorded in the form of the first derivative of the NMR absorption line by sweeping the frequency in the neighborhood of 25 MHz using a homemade NMR spectrometer with signal accumulation. The NMR measurements were carried out in the temperature range from 100 to 380 K. The upper temperature limit was set by dehydration of the samples.

Approach Used

Here we consider the effect of proton exchange on the ^{1}H NMR spectrum of the H_2O molecules, which move fast inside the zeolite framework. We restrict our consideration to the case that the frequency ν_{ex}, with which one of the water molecule

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protons is substituted by some exterior proton, and the molecular diffusion jump frequency ν_{dif} satisfy the condition

$$\nu_{ex} \ll \alpha \ll \nu_{dif} \qquad (1)$$

where $\alpha \approx 24$ kHz is the dipole–dipole interaction constant of the motionless H_2O two-spin configuration.

In the case of fast molecular diffusion in noncubic crystals the intramolecular proton–proton interaction averaged over all sites occupied by H_2O molecules results in a dipolar coupling tensor which gives rise to two resonance lines with separation depending on the crystal orientation with respect to the external magnetic field:[19,21,22]

$$2\delta = 2\lambda\alpha|3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\varphi| \qquad (2)$$

Here, θ and φ are the magnetic field spherical coordinates in the system of the tensor principal axes and λ and η are coefficients ranged from 0 to 1 depending on symmetry and peculiarities of the spatial distribution of the HH vectors of the H_2O molecules in the crystal. In triclinic crystals the averaged dipolar coupling tensor can, in principle, have any orientation relative to the crystallographic coordinate system, whereas in the cases of higher symmetry one (monoclinic case) or three (orthorhombic case) principal axes of the tensor coincide with the crystal symmetry directions. In tetragonal, trigonal, and hexagonal crystals $\eta \equiv 0$ and the rotation axis of the tensor is parallel to the main symmetry axis. However in the case considered η does not have to be zero since $R\bar{3}m$, usually accepted for chabazite, is only a pseudo space group of this crystal.[18]

The width (β) of the resonance lines is mainly determined by the fluctuations of the intramolecular interaction, resulting from molecular jumps, which contribute to β a term inversely proportional to ν_{dif},[23] and an enhancement of diffusive mobility with temperature makes the doublet structure of the spectrum more pronounced. The intermolecular proton exchange leads to an opposite effect smearing out the doublet spectrum. To evaluate this effect, let us assume, for simplicity, that H_2O is the most abundant protonated species in the crystal and the contribution of any reactant, other then H_2O, to the NMR absorption can be ignored. This assumption reduces the consideration to the solution of a well-known problem of chemical exchange between two molecular species with neighboring resonance frequencies.[24] Since each act of proton exchange may change or, with equal chance, leave unaltered mutual orientation of the nuclear spins, the NMR frequency switches from one doublet component to the other with a frequency of $\nu_{ex}/2$. And, by analogy with the case of two-position chemical exchange, we can describe the NMR spectrum in frequency units f by

$$G(f) \propto \text{Re}\left[\frac{\nu_{ex} + \beta - if}{(\beta - if)(\nu_{ex} + \beta - if) + \delta^2}\right] \qquad (3)$$

A special feature of the considered case is that δ in eq 3 is essentially anisotropic. As a consequence, the effect of proton exchange depends on the orientation of the crystal with respect to the magnetic field: at orientations corresponding to $\delta < \nu_{ex}$ the NMR doublet collapses into a single line, whose intensity enhances sharply as δ approaches zero (Figure 1). That enables one to make measurements of ν_{ex} with high accuracy. To determine ν_{ex} we simulated using eq 3 a series of spectra registered for various angles ψ of the crystal rotation around an axis perpendicular to the magnetic field. To maximize the
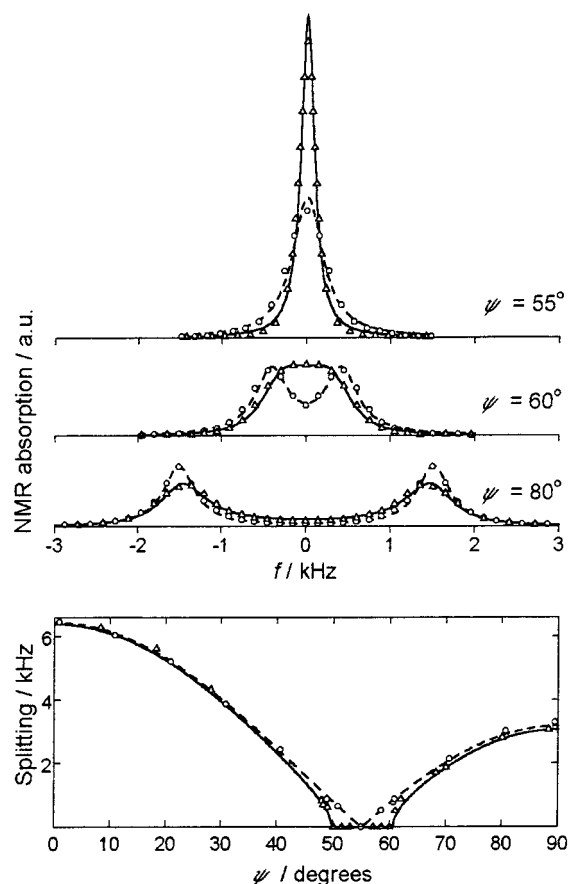

Figure 1. ^{1}H NMR absorption spectra (top) obtained by integration of the experimental derivative curves and angular dependence of the doublet splitting (bottom) for the natural chabazite single crystal at 380 K (triangles) and 290 K (circles). The corresponding curves calculated by eq 3 with $\nu_{ex} = 500$ s^{-1}, $\beta = 95$ Hz and with $\nu_{ex} \le 20$ s^{-1}, $\beta = 220$ Hz are shown by solid and dashed lines, respectively. The region of the doublet collapse ($\psi = 50$–$60°$) expands progressively as ν_{ex} increases with temperature.

range of δ variations (from 0 to $2\lambda\alpha$) the rotation axis was chosen near-perpendicular to the crystal c axis ($\psi \approx \theta$).

For powders, the hydrogen exchange frequency was determined by comparing the experimental spectra with the spectra obtained by averaging eq 3 over all chaotically oriented single crystals. In this case, as shown in Figure 2, the proton exchange, over a wide limits of ν_{ex}, results in a superposition of a narrow central peak and a smoothed doublet structure, corresponding respectively to crystallites with $\nu_{ex} > \delta$ and $\nu_{ex} < \delta$.

Results and Discussion

Proton Exchange Characteristics. The H_2O self-diffusion in the natural chabazite results in a ^{1}H NMR doublet corresponding to an effective interaction constant $\bar{\alpha} = \lambda\alpha$, which was determined to be practically constant at 1.68 ± 0.06 kHz in the temperature range 290–380 K. The η value was obtained to be 0.16 ± 0.03 that does not reconcile with the axial distribution of the H_2O molecules in the zeolite channels and thus testifies that the actual symmetry of the chabazite studied is lower than $R\bar{3}m$. On heating, the intermolecular proton exchange manifests itself in the NMR spectra starting with 330 K. The ν_{ex} values, derived from simulating the single crystal and powder spectra, are in close agreement. At 330–380 K the variation of the exchange frequency with the temperature corresponds to an Arrhenius equation (Figure 3) with activation energy $U_{ex} = 54$ kJ/mol and with preexponential factor $\nu_{ex}^\circ =$
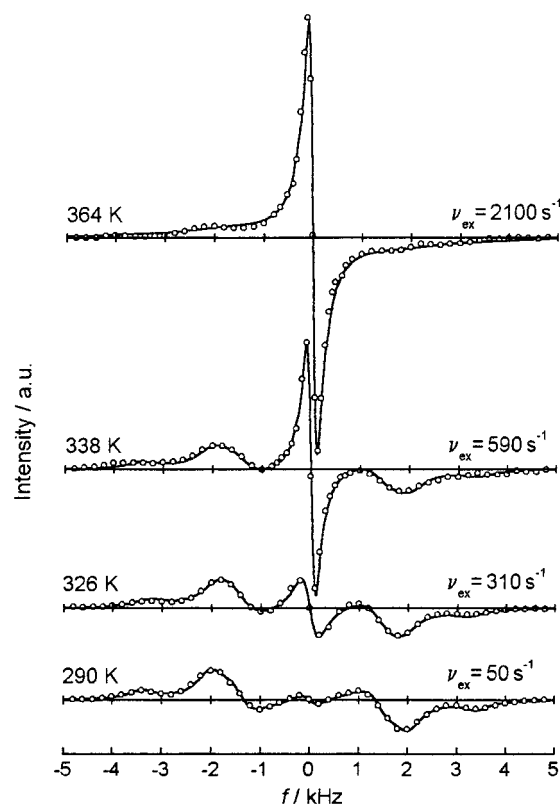
Figure 2. Experimental NMR absorption derivatives (circles) at different temperatures for the chabazite powder treated with HCl solution (pH = 4) during 3 days. The calculated spectra for different rates of proton exchange are shown as solid lines.
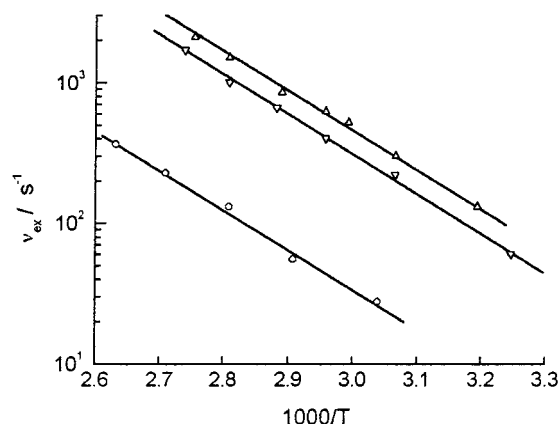
Figure 3. Arrhenius plots of the proton exchange frequency for the initial chabazite (circles) and for the same samples treated with HCl solution during 20 min (down triangles) and 3 days (triangles). The solid lines are linear fits of the data with $U_{ex} = 54$ kJ/mol and ν_{ex}° equal to 1.0×10^{10}, 9.0×10^{10}, and 1.3×10^{11} s^{-1}, respectively.

1.0×10^{10} s^{-1}. Table 1 shows that the Arrhenius parameters for proton exchange vary significantly for the samples under study. But changes in activation energy are partially offset by a change in the preexponential factor that displays a well-known compensation effect for a group of similar reactions.[25]

An intriguing result was obtained under a slight substitution of the extraframework cations for protons by the action of dilute acid solution. In this case we observed a 10-fold increase of ν_{ex} which attained 90% of its peak after standing in solution during 30−40 min. As is seen in Figure 3, this increase results from an increase of the preexponential factor only, whereas the activation energy remains unaltered. The parameters $\bar{\alpha}$, η, and β which are determined by the structural and dynamical

TABLE 1: Proton Exchange and Molecular Diffusion Arrhenius Parameters for Various Cation-Substituted Chabazites

exchanged form	U_{ex}, kJ/mol	$10^{-10}\nu_{ex}^{\circ}$, s^{-1}	U_{dif}, kJ/mol	$10^{-10}\nu_{dif}^{\circ}$, s^{-1}
K	45	0.9	24	35
Li	51	1.0	25	2.0
Ca (initial)	54[a]	1.0	24[a]	2.5[a]
Ba	55	10	21	1.0
Na	60	60	26	10

[a] These parameters remain unchanged at acidic treatment.
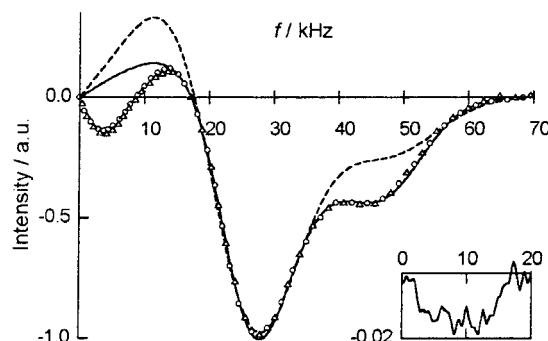
Figure 4. Half-experimental absorption derivatives for the initial chabazite (circles) and chabazite treated with HCl solution during 3 days (triangles) at 100 K. Inset: the difference of these spectra on an enlarged scale. The dashed curve corresponds to a most acceptable classical Pake function. The solid curve is a powder spectrum calculated in accordance with eqs 2 and 5 for $\lambda'\alpha = 23.4$ kHz, $\eta' = 0.06$, $\sigma_1 \approx \sigma_3 = 5.5$ kHz, and $\sigma_2 = 12$ kHz.

peculiarities of the water arrangement leave unchanged too. These results allow one to suppose that the observed proton exchange is mainly due to chemical activation of the H$_2$O molecules by zeolitic protons (HZ) the concentration of which remains unchanged at temperature variations:

$$H_2O + H'Z \leftrightarrow HH'O + HZ \qquad (4)$$
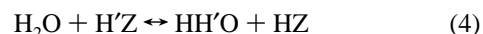
Related reactions are widely discussed for the case of the interaction of water with Brønsted acidic sites Al−O(H)−Si in various H-zeolites.[12−14] A quantity of excess protons, as chemical defects, may exist in the initial chabazite as well as in its cation-substituted forms increasing in their concentration under acidic treatment.

Active Sites. Two types of defects responsible for proton exchange would be expected: a neutral complex in which the water molecule is H-bonded to the zeolitic OH group, and an ion-pair complex in which the H$_2$O molecule is protonated and is H-bonded to the framework oxygen atoms and/or to the adjacent water molecules.[12,13] To estimate the concentration of such defects, series of the ^{1}H NMR powder spectra were recorded at 100 K where effects of proton exchange and molecular diffusion on the H−H magnetic dipolar interactions are negligible.

For all samples, the low-temperature spectra were found to be practically identical. As is seen from Figure 4, these spectra differ significantly in shape from a classical Pake doublet inherent to the H$_2$O molecules fixed in the crystal.[26] The most interesting feature is the increased intensity of the spectrum shoulder at 40−50 kHz that is usually considered to be evidence for the presence of the H$_3$O$^+$ three-spin configurations.[27,28] On the basis of a spectrum analysis described in the literature,[27] it can be deduced that the concentration of the H$_3$O$^+$ ions runs as high as 0.3−0.4/Al atom in the initial chabazite and is

unchanged on acid treatment that is in sharp contrast to the strong ν_{ex} increase.

An alternative interpretation of the low-temperature powder spectra permits one to eliminate the contradiction mentioned above. Let us consider a set of molecules fixed in symmetrically equivalent positions of the crystal. For each of them, the intramolecular dipolar interaction causes a doublet whose splitting depends on the orientation of the molecule with respect to the magnetic field. Allowing for a dynamic disordering of the HH vector, this splitting can be described by eq 2 rewritten for coefficients λ' and η' and angles θ' and φ'. At small disordering, the dynamical coefficients λ' and η' are expressible in terms of mean-square amplitudes of the two H_2O librational modes (twisting and rocking): $\lambda' = 1 - {}^3/_2(\xi_t + \xi_r)$; $\eta' = {}^3/_2(\xi_t - \xi_r)$.[29,30] The angles θ' and φ' define now the magnetic field direction in the system of the local coupling tensor whose axes coincide with the molecule principal directions. The intermolecular interactions can be accounted for by Gaussian-shaped resonance lines with the appropriate width σ. It is generally assumed that σ is an isotropic parameter, but this assumption is open to argument.[24] In particular, in H-bonded water structures, where interactions with few nearest protons may far exceed the influence of the remaining protons, the anisotropy of σ may be significant. As a first approximation, this can be represented by a general ellipsoid in the system of the principal axes of the intramolecular dipolar tensor. Considering that the positions of the nearest protons are mainly dictated by the hydrogen bonds, it is reasonable to suggest that the axes of this ellipsoid coincide closely with the molecule principal directions. Correspondingly, σ may be written as

$$\sigma^2 = \sigma_1{}^2 \cos^2 \theta' + \sigma_2{}^2 \sin^2\theta' \cos^2 \varphi' + \sigma_3{}^2 \sin^2 \theta' \sin^2 \varphi' \quad (5)$$

Further, integrating a function represented by the two Gaussians over a solid angle, we get a powder spectrum specified by the following five parameters: $\lambda'\alpha$; η'; σ_1; σ_2; σ_3. As may be seen from Figure 4, a proper choice of these parameters allows one to obtain a good fit to the experimental spectra without invoking the effect of H_3O^+ ions on the NMR absorption.

Thus we can suppose that, actually, the H_3O^+ ions are found in a minor amount and the overwhelming majority of protons are distributed among the H_2O and OH species. The latter manifests itself in the range 0–13 kHz: from the discrepancy between the experimental and calculated spectra their amount was estimated to be about 1.5% of full proton content for all samples. Acid treatment leads to a faintly visible buildup of the spectral intensity in the hydroxyl region (inset in Figure 4) that corresponds to an increase of the ratio HZ/Al of 0.02 ± 0.01. Bearing in mind that the acid treatment is accompanied with ν_{ex} strong enhancement, it is reasonable to associate just these excess protons with the active OH groups. The remainder of the detected hydroxyls can be associated with chemically inactive defects represented, apparently, by surface OH groups. Assuming that ν_{ex} is proportional to the concentration of the active sites, it can be estimated that in the initial chabazite the ratio HZ/Al is of order of 10^{-3}.

From the above reasoning it may be safely suggested that the stable state of the defects of interest corresponds to a neutral adsorption structure, whereas the ion-pair complex is the most likely transition state for the proton exchange between hydroxyls and water molecules. The ability of each water molecule to enter into the proton transfer reactions with the sparsely distributed hydroxyls arises primarily from an intense H_2O molecular exchange between different structural positions.

H_2O Self-Diffusion. To examine the H_2O diffusive mobility we considered the evolution of the ^{1}H NMR spectra in the range 150–330 K where their shapes appear to be essentially dependent on ν_{dif}. Using known relations between the NMR line width and a frequency characterizing molecular mobility,[23,31] the H_2O self-diffusion activation energy was found to be about of half the exchange barrier for all samples under study. A comparison between the activation parameters tabulated in Table 1 shows that in the temperature range 300–380 K the H_2O molecule executes, on average, about 10^5 jumps between different structural positions for each act of the proton-transfer reaction. Therefore, even though the ratio HZ/H_2O is of order of 10^{-3}, the molecule has a chance to make many contacts with zeolitic protons prior to one reaction will take place. In such conditions, ν_{ex} can be expressed in terms of the local exchange characteristics U_i and ν_{i}°, determined for each of the H_2O structural positions, which are in the immediate contact with the active acid site:

$$\nu_{ex} = \sum p_i \nu_i^{\circ} \exp(-U_i/kT) \approx \bar{\nu}^{\circ} \exp(-U_{ex}/kT) \sum p_i \quad (6)$$

where p_i is the probability that a given molecule will appear in the ith position. In the case of a highly hydrated state of the zeolite, the sum of p_i agrees closely with the HZ/H_2O ratio. Then, with the assessment of the concentration of the active sites in the initial chabazite, the preexponential factor $\bar{\nu}^{\circ}$, which characterizes the proton transfer within the local adsorption structure, can be estimated to be of the order of 10^{13} s^{-1}. However, this estimation must be used with great caution since (i) a heterogeneity of proton acidity between different active sites may induce a substantial spread in the local activation parameters and (ii) p_i may, actually, be temperature dependent. Note that both these effects can be responsible for the above-mentioned compensation effect.[32]

Charge Transfer. In the context of an assumption that the neutral complex OH$\cdots$H$_2$O corresponds to the only minimum on the potential energy surface, the proton exchange discussed here represents the proton transfer from the one zeolite oxygen atom to the water molecule and the subsequent or simultaneous return of one of the molecular protons to the other oxygen site. This means a certain delocalization of the acid sites and implies a charge mobility wherein the excess protons migrate between different oxygen sites via water molecules with a characteristic frequency $\nu(H) = \bar{\nu}^{\circ} \exp(-U_{ex}/kT)$. It was interesting to compare this mobility with the extraframework cation mobility, which was examined with ^{23}Na NMR. In the range 300–400 K we observed an evolution of spectra, induced by the Na$^+$ diffusion. From the temperature dependence of the line width the diffusion activation energy was determined to be 45(3) kJ mol^{-1} with the preexponential factor of 10^{13} s^{-1}. On the basis of this result and the foregoing estimations, metal ions can be expected to be more mobile charge carriers as compared to protons. But it should be noted that the discussed mechanism is not the only path of proton migration. The alternative may be the direct proton exchange between neighboring oxygen sites.[7,33]

Conclusions

There are a variety of spectroscopic techniques available for the investigation of the proton motion in solids on different characteristic time scales. In this paper we have demonstrated a simple wide-line NMR method to measure, to a high accuracy, the rate of the proton exchange in water molecules incorporated in crystals which can be applied when the average time between

events of H-exchange lies in the range of $10^{-1}-10^{-4}$ s. The method will, presumably, be applicable for studying various hydrated microporous crystals. The conditions for such measurements are the following: (i) a high rate of molecular diffusion; (ii) a noncubic symmetry of the crystal that prevents the full suppression of the intramolecular nuclear spin interactions by the molecular motion.

We have studied the proton exchange in the hydrated zeolite chabazite and in its cation-substituted forms. We have interpreted this exchange as the reversible proton-transfer reaction between water molecules and a small amounts of the excess protons (de)localized on the bridging oxygen atoms of the zeolite framework. The proton-transfer energies have been found below the energies corresponding to the proton transfer between Brønsted acidic sites and various hydrocarbon molecules, which lie in the range from 60 to 120 kJ/mol.[6,11] At the same time, the barriers observed are significantly higher than the value of about 10 kJ/mol that can be expected from the ab initio calculations performed for a cluster with one water molecule per acidic site.[12,13]

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