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Characterization of sodium cations in dehydrated faujasites and zeolite EMT by ^{23}Na DOR, 2D nutation, and MAS NMR

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Abstract

Sodium cations localized at crystallographically distinct cation sites in dehydrated zeolites were characterized using ^{23}Na double rotation, two-dimensional nutation, and magic-angle-spinning nuclear magnetic resonance spectroscopy. The new DOR NMR technique has been applied at different magnetic field strengths to determine the quadrupole parameters of the overlapping quadrupole patterns. In the NMR spectra of dehydrated NaY and NaEMT two signals of sodium cations were identified, a low-field gaussian line at -12 ± 1 ppm and a high-field quadrupole pattern, with an isotropic chemical shift of -8 ± 1 ppm and a quadrupole coupling constant of about 4 MHz. By comparison of the ^{23}Na MAS NMR intensities of these signals with the population of the cation sites determined by XRD and by calculation of the electric field gradients, the former signal was attributed to sodium cations at the sites SI and the latter one to sodium cations at the sites SI′ as well as SII in faujasite and zeolite EMT. This assignment has further been confirmed by ^{23}Na MAS NMR studies of dehydrated HNaY and BaNaY zeolites.

Keywords: ^{23}Na DOR NMR; 2D nutation; quadrupole coupling constant; sodium cations; zeolites

Introduction

The characterization of the location of cations in zeolites plays an important role in determining the adsorption and catalytic properties of zeolites. XRD has revealed different sites for cation location in the faujasite and EMT structure which are presented in Fig. 1. A number of papers [1–7] have been published in the last decade using various ^{23}Na NMR techniques to study sodium cations in hydrated and dehydrated zeolites. While the lineshapes and chemical shifts of ^{23}Na NMR signals of hydrated zeolites are influenced by the sodium mobility [1–3], studies of dehydrated zeolites [6,7] yield quadrupole patterns due to sodium cations localized at crystallographically distinct cation sites. The dramatic improvement of spectral resolution by the double-rotation (DOR) NMR technique yields narrow, well-separated lines for the nuclei under study. The different local cation surroundings by framework oxygen atoms cause different electric field gradients (EFG) at these sites which are reflected by the respective quadrupole coupling constants, Q_C, and the asymmetry parameter η of the EFG. Both Q_C and η can be determined using DOR NMR at different magnetic field strengths and the simulation of magic-angle-spinning (MAS) NMR spectra [8–10]. The intensities of the quadrupole patterns allow the determination of the population of crystallographically distinct sites by sodium cations. In addition, it has been shown that two-dimensional nutation NMR is an efficient technique to separate quadrupole and chemical shift interactions [4–6]. The aim of the

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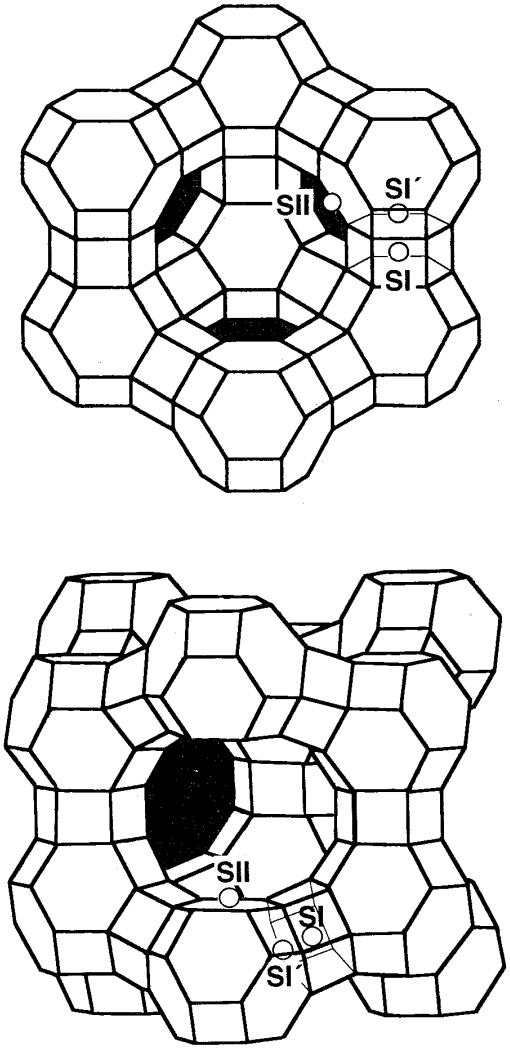

Fig. 1. Structure of faujasite (top) and zeolite EMT (bottom) and cation sites SI, SI′, and SII, according to ref. 19.

present paper is to illustrate the advantage of a combined application of the various solid-state NMR techniques, *i.e.*, DOR, 2D nutation, and MAS NMR, for a detailed characterization of sodium cations in the cubic faujasite (FAU) and hexagonal zeolite EMT.

Experimental

The NaY zeolite used in the present study is a commercial product (Union Carbide Corp., Tarrytown, NY, USA) with the unit cell composition $Na_{53.3}Al_{53.3}Si_{138.7}O_{384} \cdot xH_2O$. Cation exchanged samples were prepared at 343 K using an aqueous solution of $Ba(NO_3)_2$ in two steps with calcination (433 K) in air after the first step yielding an exchange degree of 83% of Na^+ against Ba^{2+} (BaNaY), and at ambient temperature using a solution of NH_4NO_3 yielding an exchange degree of 52% (after activation, sample HNaY). After the exchange procedures the zeolites were washed and dried at 373 K. NaEMT was synthesized as described in ref. 11. The composition as determined by inductively-coupled plasma atomic emission spectroscopy is: $Na_{20.4}Al_{20.4}Si_{75.6}O_{192} \cdot xH_2O$. X-ray powder diffraction revealed the high crystallinity of the as-synthesized product. The n_{Si}/n_{Al} ratio of the framework, as determined by ^{29}Si MAS NMR, is 2.6 for NaY and 3.7 for NaEMT. No extra-framework aluminium could be observed in the ^{27}Al MAS NMR spectra of the hydrated samples. The activation was carried out by heating a 200-mg zeolite sample in a glass tube with 6-mm inner diameter under vacuum at a heating rate of 10 K/h. After keeping the sample for 2 h at 673 K the material was evacuated to below 10^{-2} Pa for 12 h and sealed. Before the NMR measurements the samples were filled into the MAS and DOR rotors under dry nitrogen gas in a glove box. No rehydration of the zeolites in the closed rotors has been observed during 24 h.

The ^{23}Na NMR experiments were carried out on Bruker MSL 300 and MSL 400 spectrometers at Larmor frequencies of $\nu_{L1} = 79.4$ MHz and $\nu_{L2} = 105.8$ MHz, respectively. For the ^{23}Na MAS NMR studies a standard 4-mm double-bearing Bruker MAS probe with rotation frequencies of about 9 kHz was used and single pulse excitation of 0.7 μs corresponding to $\pi/8$ flip angles was applied. A minimum of 2000 scans was accumulated for each MAS NMR spectrum with a recycle time of 500 ms. The MAS NMR spectra were simulated on the Bruker computer Aspect 3000 using the program Powder. The 2D nutation experiments were carried out at a resonance fre-

quency of $\nu_{L2} = 105.8$ MHz, a radio-frequency field strength of 125 kHz, and simultaneous application of MAS at a rotation frequency of 9 kHz. To increase the radio-frequency field homogeneity the volume of the sample in the MAS rotors was reduced to about 50% and located in the center of the coil. For each 2D nutation NMR spectrum 64 rows of 1024 data points were collected with t_1 incremented in 1-μs steps and the first row being zeroed. The free induction decays of 2000 scans were doubly Fourier transformed in the magnitude mode after the last one was subtracted from all the others. The DOR NMR studies were carried out using the Bruker double-rotation probe. According to the method published by Samoson and Lippmaa [12], rotor synchronized single-pulse excitation was used to suppress the odd-numbered DOR sidebands. All

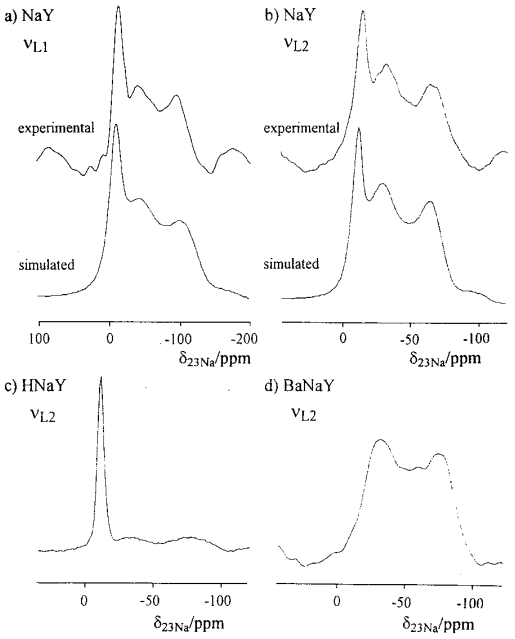

Fig. 2. ^{23}Na MAS NMR spectra of dehydrated (673 K) NaY (a, b), HNaY (c) and BaNaY (d) zeolites, recorded at a Larmor frequency of $\nu_{L1} = 79.4$ MHz (a) and $\nu_{L2} = 105.8$ MHz (b, c, d). The simulation of the MAS NMR spectra (a) and (b) were carried out using the parameter Q_C and η given in Table 1.

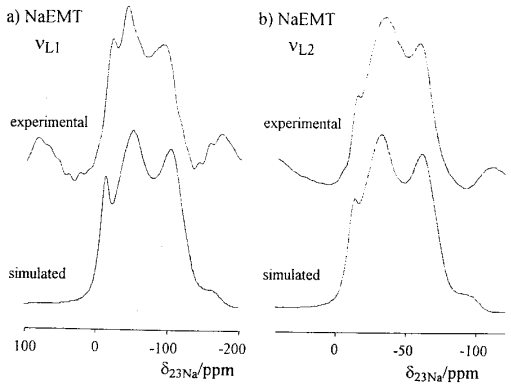

Fig. 3. ^{23}Na MAS NMR spectra of dehydrated (673 K) NaEMT zeolite, recorded at Larmor frequencies of $\nu_{L1} = 79.4$ MHz (a) and $\nu_{L2} = 105.8$ MHz (b). The simulation of the MAS NMR spectra were carried out using the parameters Q_C and η given in Table 1.

^{23}Na NMR shifts are referenced to an external standard of solid NaCl.

Results

MAS NMR studies

The ^{23}Na MAS NMR technique has been applied to study sodium cations in dehydrated NaY, HNaY, and BaNaY zeolites and in dehydrated zeolite NaEMT (Figs. 2 and 3). In the low-field range (to positive chemical shifts) of the ^{23}Na MAS NMR spectra of dehydrated NaY and NaEMT a line at about -13 ppm is observed which shows no significant shift variation compared to the spectra recorded at ν_{L1} and ν_{L2} (Figs. 2a and 2b). In the spectra of NaEMT (Figs. 3a and 3b) this signal appears as a shoulder at about -14 ppm. The high-field range of all spectra is dominated by a pattern with two resolved singularities. For NaY these singularities were shifted from -41.1 to -31.3 ppm and from -96.2 to -63.4 ppm on increasing the Larmor frequency from ν_{L1} to ν_{L2}. A similar behaviour is observed in the spectra of NaEMT where the singularities of the high-field patterns shift from -36.8 to -32.8 ppm and from -85.9 to -57.9

ppm at the two different Larmor frequencies. For attributing the ^{23}Na NMR signals to cations at crystallographically distinct sites an exchange of sodium cations in NaY against protons and Ba^{2+} has been carried out. As illustrated in Fig. 2c the replacement of 52% of the sodium cations by protons causes a strong decrease of the relative intensity of the high-field pattern of the dehydrated zeolite while the low-field line remains with a strong intensity. In contrast, the spectrum of the dehydrated BaNaY (Fig. 2d) consists only of a high-field pattern with singularities at −31.4 and −70.8 ppm.

DOR NMR studies

^{23}Na DOR NMR has been applied to the dehydrated zeolites NaY and NaEMT (Figs. 4 and 5). It is well known, that the experimentally observed line positions δ_n^{DOR} are shifted from the isotropic chemical shift, δ_{iso}, by a second-order quadrupolar shift, σ_{qs}, which is a function of the external magnetic field strength and the quadrupole interaction parameters Q_C and η. The theoretical background has been discussed by Müller [13] and successfully applied to interpret the ^{27}Al DOR NMR spectra of aluminate sodalites [8] and the ^{17}O DAS (dynamic-angle spinning) NMR spectra of various silicates [14]. δ_{iso} can be calculated from the line position δ_1^{DOR} and δ_2^{DOR} of the DOR NMR spectra measured at different Larmor frequencies ν_{L1} and ν_{L2} according to eqn. (1) which has been derived from the expressions given in ref. 8:

$$\delta_{iso} = \frac{\delta_1^{DOR} K_2 - \delta_2^{DOR} K_1}{K_2 - K_1} \quad (1)$$

using

$$K_n = \frac{3 \cdot 10^6 \cdot [I(I+1) - 3/4]}{40 \cdot \nu_{Ln}^2 \cdot I^2 (2I-1)^2} \quad (2)$$

with $I = 3/2$ for ^{23}Na, $n = 1$, 2 and the Larmor frequencies ν_{Ln} in MHz. In addition, the quadru-

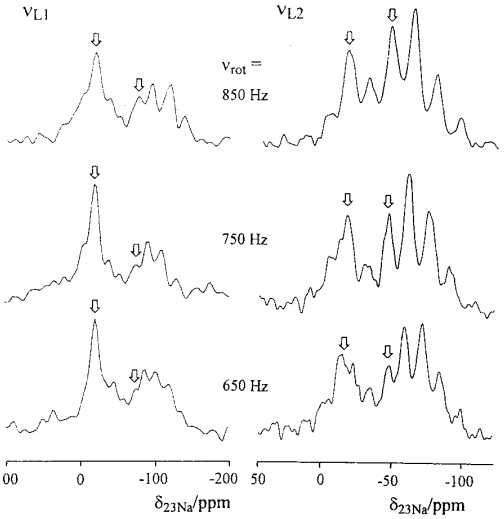

Fig. 5. ^{23}Na DOR NMR spectra of dehydrated (673 K) NaEMT zeolite, recorded at Larmor frequencies of $\nu_{L1} = 79.4$ MHz and $\nu_{L2} = 105.8$ MHz and using rotor-synchronized pulse excitation at different DOR frequencies ν_{rot}. The arrows indicate the central lines of the DOR sideband patterns.

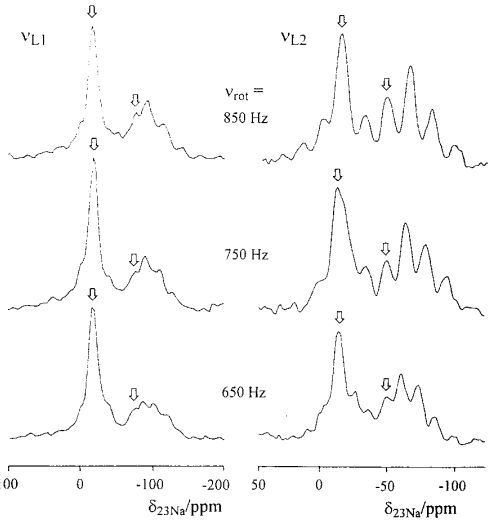

Fig. 4. ^{23}Na DOR NMR spectra of dehydrated (673 K) NaY zeolite, recorded at Larmor frequencies of $\nu_{L1} = 79.4$ and $\nu_{L2} = 105.8$ MHz and using rotor-synchronized pulse excitation at different DOR frequencies ν_{rot}. The arrows indicate the central lines of the DOR sideband patterns.

pole coupling constant $Q_C^* = Q_C \cdot \sqrt{(1+\eta^2/3)}$ can be estimated [9] by

$$Q_C^* = \sqrt{\frac{\delta_1^{DOR} - \delta_2^{DOR}}{K_2 - K_1}} \quad (3)$$

Since in the present study the odd-numbered spinning sidebands are suppressed by rotor-synchronized pulse excitation [12], the ^{23}Na DOR NMR spectra of dehydrated NaY and NaEMT consist of patterns with sidebands separated by the two-fold spinning frequency of the outer rotor which yields a considerable increase in resolution. In order to identify the central line of the DOR patterns, measurements with rotation frequencies of the outer DOR rotor of 650, 750 and 850 Hz were carried out (Figs. 4 and 5). For both samples, NaY and NaEMT, two lines were identified, which show no variation of the line positions at different spinning frequencies and are indicated by arrows in Figs. 4 and 5. In the low-field range of the ^{23}Na DOR NMR spectra of dehydrated NaY recorded at $\nu_{L1} = 79.4$ MHz and $\nu_{L2} = 105.8$ MHz a line appears at -13 ppm. The DOR

TABLE 1

Line positions δ_{exp} (accuracy ± 1.0 ppm) in the ^{23}Na DOR, 2D nutation, and MAS NMR spectra of dehydrated faujasites and zeolite NaEMT at different Larmor frequencies, ν_L, and quadrupole coupling constants, Q_C, asymmetry parameter, η, isotropic chemical shifts, δ_{iso}, and relative intensities derived by the simulation of quadrupole patterns (MAS) or using eqns. (1) and (3) (DOR)

Technique	ν_L (MHz)	δ_{exp} (ppm)	Q_C (MHz)	η	δ_{iso} (ppm)	Relative intensity (%)	
						exp.	corr.
NaY							
DOR	79.4	−14.6					
		−78.0					
	105.8	−13.4					
		−48.0	4.2 [b]		−9		
nutation	105.8	−12.8	< 0.25				
		−32.4 [a], −66.0 [a]	> 0.25				
MAS	79.4	−14.7	0	0	−11		
		−41.1 [a], −96.2 [a]	4.2	0.25	−7		
	105.8	−13.2	0	0	−11	29	6
		−31.3 [a], −63.4 [a]	4.2	0.25	−7	71	94
HNaY							
MAS	105.8	−11.5	0	0		72	29
		−33.7 [a], −70.5 [a]	4.8	0.25		28	71
BaNaY							
MAS	105.8	−31.4 [a], −70.8 [a]	4.8	0.26		100	
NaEMT							
DOR	79.4	−14.8					
		−75.0					
	105.8	−14.2					
		−46.0	4.1 [b]		−9		
nutation	105.9	−34.2 [a], −55.6 [a]	> 0.25				
MAS	79.4	−14.6	0	0	−11		
		−36.8 [a], −85.9 [a]	4.1	0.3	−7		
	105.8	−12.8	0	0	−11	14	2.5
		−32.8 [a], −57.9 [a]	4.1	0.3	−7	86	97.5

[a] Peak of the quadrupole pattern. [b] $Q_C \cdot \sqrt{(1+\eta^2/3)}$.

NMR spectra of NaEMT show a corresponding line at −14 ppm but with lower intensity. Only small changes in the positions of these lines are observed in the DOR and MAS spectra measured at different field strengths (see Table 1), indicating a very small or vanishing quadrupole interaction of the corresponding sodium cations. The high-field range (to negative chemical shifts) of the ^{23}Na DOR NMR spectra of NaY, recorded at Larmor frequencies of ν_{L1} and ν_{L2}, is dominated by a sideband pattern with a central line at −78.0 and −48.0 ppm, respectively. In the corresponding spectra of NaEMT this line was identified at −75.0 and −46.0 ppm, respectively. A summary of the above-mentioned line positions is given in Table 1. Using the resonance positions of the high-field signals of NaY and NaEMT recorded at ν_{L1} and ν_{L2}, quadrupole coupling constants Q_C^* of 4.2 and 4.1 MHz [eqn. (3)], respectively, and a isotropic chemical shift of $\delta_{iso} = -9$ ppm [eqn. (1)] could be estimated.

2D nutation

The stacked plots of the 2D nutation spectra of the dehydrated zeolites NaY and NaEMT are shown in Fig. 6. The frequencies ν_1 of the signals in the F1 dimension (tilted axis) of these spectra depend on the quadrupole frequency, $\nu_q = 3 \cdot Q_C/[2I(2I-1)]$, of the resonating nuclei and are independent of the chemical shift of the corresponding signals in the F2 dimension. According to Kentgens *et al.* [15] three different cases can be distinguished:

(1) $\nu_q \ll \nu_{rf}$, which yields a signal in the F1 dimension at the nutation frequency $\nu_1 = 1\nu_{rf}$,

(2) $\nu_q \gg \nu_{rf}$, a signal appears at the nutation frequency $\nu_1 = (I + 1/2) \cdot \nu_{rf}$, *i.e.*, for ^{23}Na nuclei with $I = 3/2$ follows $\nu_1 = 2\nu_{rf}$, and

(3) $\nu_q \cong \nu_{rf}$, with a broad pattern in the range between $\nu_1 = 1\nu_{rf}$ and $2\nu_{rf}$.

In the 2D nutation spectrum of the dehydrated NaY (Fig. 6, top) a signal at $\nu_1 = 1\nu_{rf}$ appears in the F1 dimension which corresponds to a line the F2 dimension at about −13 ppm. In addition, a peak is observed at $\nu_1 = 2\nu_{rf}$ corresponding to a pattern with singularities at $\delta_{^{23}Na} = -32.4$ and −66.0 ppm. Since for the first of the above-mentioned signals ($\nu_1 = 1\nu_{rf}$) the condition $\nu_q \ll \nu_{rf}$ (case *1*) is fulfilled, the sodium cations giving rise to this signal are characterized by a quadrupole frequency smaller than the applied radio-frequency field strength of $\nu_{rf} = 125$ kHz, *i.e.*, by a quadrupole coupling constant smaller than 0.25 MHz. In contrast, the pattern with singularities at $\delta_{^{23}Na} = -32.4$ and −66.0 ppm is due to sodium nuclei with a quadrupole frequency $\nu_q \gg \nu_{rf}$ (case *2*) corresponding to $Q_C \gg 0.25$ MHz. The 2D nutation spectrum of the dehydrated NaEMT (Fig. 6, bottom) consists in the F1 dimension of only one peak at $\nu_1 = 2\nu_{rf}$ corresponding to a pattern with singularities at $\delta_{^{23}Na} = -34.2$ and −55.6 ppm. As mentioned above for NaY, this signal at $\nu_1 = 2\nu_{rf}$ is due to sodium cations with a quadrupole coupling constant $Q_C \gg 0.25$ MHz. In the range of $\nu_1 = \nu_{rf}$ only negligible intensities could be observed in the spectrum of NaEMT which were not attributed to distinct signals.

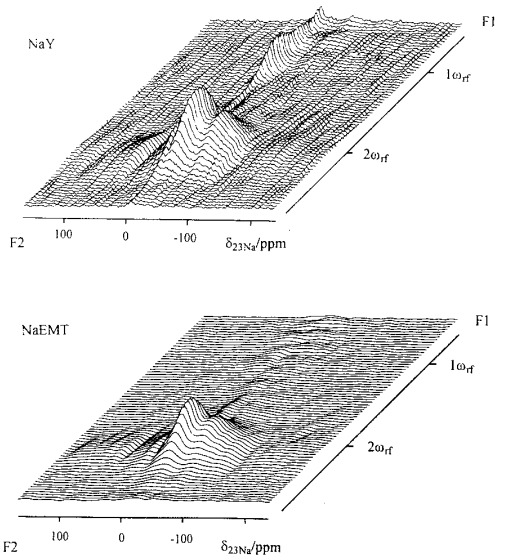

Fig. 6. Two-dimensional nutation NMR spectra of sodium cations in dehydrated (673 K) NaY (top) and NaEMT (bottom). The spectra were recorded with a rf field strength of $\omega_{rf}/2\pi = 125$ kHz and doubly Fourier transformed in the magnitude mode.

Discussion

The application of various techniques of solid-state NMR for studying sodium cations in dehydrated NaY and NaEMT permits a detailed characterization of the quadrupole interactions of these nuclei. The small changes of the position of the line at about −13 ppm observed in the DOR and MAS NMR spectra recorded at different magnetic field strengths indicate a small or vanishing quadrupole interaction of the corresponding sodium cations. In agreement with this conclusion, the 2D nutation NMR spectroscopy yields a quadrupole coupling constant of the corresponding sodium nuclei of $Q_C \ll 0.25$ MHz. Hence, a contribution of the quadrupole interaction to the shift of this signal can be neglected and the experimentally observed ^{23}Na NMR shift corresponds to the isotropic chemical shift, δ_{iso}. In contrast to the spectra published by Jelinek *et al.* [7], in the high-field range of the ^{23}Na DOR NMR spectra of dehydrated NaY a well-resolved sideband pattern with a single central line appears. The spectra in Fig. 4 illustrate that this central line does not coincide with the peak of the highest intensity as proposed by Jelinek *et al.* [7]. Using the ^{23}Na DOR NMR shift data of this line recorded at different Larmor frequencies, the quadrupole coupling constant is determined to be about 4.2 MHz. The corresponding isotropic chemical shift was estimated to be about −9 ppm. The 2D nutation NMR experiments yield a quadrupole coupling constant of this signal of $Q_C \gg 0.25$ MHz which agrees with the results derived by DOR NMR. Considering these parameters, the simulation of ^{23}Na MAS NMR spectra of the NaY and NaEMT zeolites was started with $Q_C = 0$ MHz (gaussian line) and $\delta_{iso} = -13$ ppm for the low-field line, and $Q_C =$ 4.2 MHz (quadrupole pattern) and $\delta_{iso} = -9$ ppm for the high-field pattern. The best fit of the experimental and simulated spectra of dehydrated NaY (Figs. 2a and 2b) was obtained using $Q_C = 0$ MHz and $\delta_{iso} = -11$ ppm for the low-field line, and $Q_C = 4.2$ MHz, $\eta = 0.25$, and $\delta_{iso} = -7$ ppm for the high-field pattern (see Table 1). The best fit of the high-field pattern of NaEMT (Figs. 3a and 3b) was achieved with the parameters $Q_C = 4.1$ MHz, $\eta = 0.3$ and $\delta_{iso} = -7$ ppm. The simulation of the ^{23}Na MAS NMR spectra of dehydrated HNaY and BaNaY zeolites was successfully carried out using the above-mentioned parameters of NaY but a quadrupole coupling constant of the high-field pattern of $Q_C = 4.8$ MHz.

In principle, the populations of the distinct cation sites by sodium can be determined from the intensities of the corresponding lines in the ^{23}Na NMR spectra. However, for large quadrupole interactions only the intensity of the central $+1/2 \leftrightarrow -1/2$ transition is experimentally observed (selective excitation) which amounts to 40% of the total intensity of the central and $\pm 3/2 \leftrightarrow \pm 1/2$ satellite transitions. A further intensity correction results from the fact that only a certain part of the intensity of the central transition is observed in the experimental spectrum. According to the method described by Massiot *et al.* [16] the experimentally observed intensity contribution from the MAS line to the total intensity of the central transition can be determined graphically if the quadrupole frequency, ν_q, the MAS frequency, ν_{rot}, and the Larmor frequency, ν_L, are known. With the corresponding data for the high-field quadrupole pattern of the NaY and EMT zeolites ($\nu_q = 2.1$ MHz, $\nu_{rot} = 9$ kHz and $\nu_L = 105.8$ MHz), it follows that only 16% of the central transition intensity is observed in the spectra. Hence, the measured intensity has to be corrected by a factor of $1/0.16 = 6.25$. Due to the small quadrupole interaction of the low-field line, all transitions contribute to the observed intensity (non-selective excitation) and no intensity correction is required.

To assign the experimentally observed NMR signals to sodium cations at crystallographically distinct sites, the corrected ^{23}Na MAS NMR intensities were compared with the site population determined by X-ray diffraction. Table 2 summarizes the population of the sites SI in the center of the hexagonal prisms, of the sites SI′ close to the center of the six-ring windows in the sodalite cages (or β-cages), and of the sites SII close to the center of the six-ring windows in the supercages (see Fig. 1). In accordance with the literature data [17,18], a significant population of

TABLE 2

Population of cation sites SI and SI′ + SII by sodium in dehydrated faujasites and zeolite EMT as obtained from XRD (literature data), and ^{23}Na NMR (this work)

Sample	Total Na content (Na/UC)	Technique	SI (Na/UC)	SI′ + SII (Na/UC)
NaY	57.0	XRD [17]	7.7	42.8
	53.3	NMR	3.2	50.1
HNaY	27.0	XRD [23]	7.4	20.4
	27.7	NMR	8.0	19.7
BaNaY	16.0	XRD [22]	–	3.7
	9.1	NMR	–	9.1
NaEMT	21.1	XRD [19]	1.4	17.9
	20.4	NMR	0.5	19.9

the sites SIII in the faujasite cages of the dehydrated NaY was excluded. It has to be noted that in the zeolite structures under study two kinds of hexagonal prisms exist, one with point symmetry *2/m* which is characteristic for all hexagonal prisms of faujasites and for 2/3 of all hexagonal prisms of EMT zeolites and a second with the point symmetry $\bar{6}m2$, characteristic of 1/3 of all hexagonal prisms of EMT zeolites. Since for the latter type a vanishing cation population was found by Lievens *et al.* [19], only hexagonal prisms with point symmetry *2/m* are considered in Table 2 and in the following discussion.

As shown by XRD (Table 2) the exchange of 52% of the sodium cations by protons (HNaY) causes a decrease of about 50% of the sodium cations at SI′ and SII while the population of SI remains at the value determined for NaY zeolites. In the ^{23}Na MAS NMR spectra a decrease of the intensity of the high-field pattern was observed from a value corresponding to 50.0 Na/UC (NaY) to a value corresponding to 19.6 Na/UC (HNaY) while the low-field line shows an increase of intensity. Comparing the XRD and NMR data, the low-field line has to be attributed to sodium cations at SI and the high-field pattern to sodium cations localized at SI′ as well as at SII. The same assignment follows considering the ^{23}Na MAS NMR spectrum of dehydrated BaNaY which shows that barium exchange causes a removal of all sodium cations from SI (XRD data in Table 2) and consequently a disappearance of the low-field line at about −13 ppm. In addition, the population of sodium cations at SI of NaEMT (X-ray data in Table 2) corresponds with the weak intensity of the low-field shoulder observed in the MAS NMR spectra of NaEMT at about −14 ppm and with the absence of a peak at $\nu_1 = 1\nu_{rf}$ in the 2D nutation NMR spectrum of NaEMT (Fig. 6, bottom).

Sodium cations at SI have a six-fold oxygen coordination to three framework oxygens of each of the two six-ring windows of the hexagonal prisms with sodium/oxygen distances of 6 × 2.65 Å [18,19]. For the octahedral coordination of cations in hexagonal prisms with point symmetry *2/m* the electric field gradients and, therefore, the quadrupole coupling constants [20,21] are zero, which agrees with $Q_C \approx 0$ MHz as observed for the sodium cations of the low-field line at about −13 ppm. In dehydrated NaY the cations at the sites SI′ and SII have similar sodium/oxygen coordinations [18,19]. Using a point-charge model [20] with oxygen charges between −0.8 and −1.1 e and the XRD data of the dehydrated (723 K) NaY [17], the quadrupole coupling constants of sodium cations localized at SI′ and SII were estimated to be between 3.4 and 5.6 MHz. Hence, the experimentally determined quadrupole coupling constant of about 4 MHz of the high-field pattern agrees well with the values derived from the theoretical model. For sodium cations localized close to the center of the six-ring windows in dehydrated NaA zeolites Tijink *et al.* [6] determined a quadrupole coupling constant of $Q_C = 5.8$ MHz. Since the type of coordination of these cations is similar to that of sodium cations at SI′ and SII in faujasites (see ref. 18), the quadrupole coupling constant published by Tijink *et al.* [6] is, as well, in reasonable agreement with the values of Q_C determined in this study of dehydrated NaY and NaEMT zeolites.

Conclusions

The ^{23}Na MAS NMR spectra of dehydrated NaY and NaEMT zeolites show broad and com-

plex patterns which are difficult to analyze. However, two distinct signals could clearly be identified in the corresponding DOR NMR spectra measured with rotor-synchronized pulse excitation at different spinning speeds of the outer rotor. Q_C of about zero and about 4 MHz, respectively, and δ_{iso} of -12 ± 1 and -8 ± 1 ppm, respectively, have been derived for the two lines from DOR spectra recorded at different magnetic field strengths and subsequent simulation of the MAS lineshapes. The presence of two lines characterized by very small and strong quadrupole interactions could also be confirmed by two-dimensional nutation NMR.

Electric field gradient calculations by a point-charge model yield Q_C of about zero for sodium cations in the SI position, *i.e.*, in the center of the hexagonal prism, while Q_C in the range of 3.4 to 5.6 MHz is obtained for sodium cations localized in the SI′ or SII positions, *i.e.*, close to the center of the six-ring windows in the β-cages or supercages, respectively. Thus, the line characterized by a vanishing value of Q_C appearing in the MAS and DOR spectra as a gaussian line at low field is assigned to sodium cations in the SI position, while the line with Q_C of about 4 MHz yielding the high-field quadrupolar lineshape in the MAS spectrum and the sideband pattern in the DOR spectrum has to be attributed to sodium cations residing at both the SI′ and SII sites. This assignment is confirmed by comparison of the (corrected) line intensities of the ^{23}Na MAS NMR spectra with the SI and SI′ + SII site populations of dehydrated zeolites NaY, HNaY, BaNaY, and NaEMT as derived from XRD studies.

The results of this study demonstrate that the combined application of ^{23}Na MAS and DOR NMR techniques opens new possibilities to study the cation distribution in zeolites and to obtain valuable information on the coordination properties of the cations by the oxygen atoms of the zeolite framework. It should be emphasized, however, that rotor-synchronized pulse excitation, variable spinning speeds of the double rotor and measurements at at least two different magnetic field strengths are prerequisites for a reliable interpretation of the ^{23}Na DOR NMR spectra of dehydrated sodium zeolites.

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References

1 B. Welsh and S.L. Lambert, in W.H. Flank and T.E. Whyte (Eds.), *Perspectives in Molecular Sieve Science*, Am. Chem. Soc., Washington, DC, 1988, p. 33.
2 R. Challoner and R.K. Harris, *Zeolites*, 11 (1991) 265.
3 H.K. Beyer, G. Pal-Borbely and H.G. Karge, *Microporous Mater.*, 1 (1993) 67.
4 C.-F. Lin and K.-J. Chao, *J. Phys. Chem.*, 95 (1991) 9411.
5 G. Engelhardt, J.-Ch. Buhl, J. Felsche and H. Förster, *Chem. Phys. Lett.*, 153 (1988) 332.
6 G.A.H. Tijink, R. Janssen and W.S. Veeman, *J. Am. Chem. Soc.*, 109 (1987) 7301.
7 R. Jelinek, S. Özkar and G.A. Ozin, *J. Am. Chem. Soc.*, 114 (1992) 4907; and *J. Phys. Chem.*, 96 (1992) 5949.
8 G. Engelhardt, H. Koller, P. Sieger, W. Depmeier and A. Samoson, *Solid State Nucl. Magn. Reson.*, 1 (1992) 127.
9 G. Engelhardt and W.S. Veeman, *J. Chem. Soc., Chem. Commun.*, (1993) 622.
10 M.P.J. Peeters, J.W. de Haan, L.J.M. van de Ven and J.H.C. van Hooff, *J. Chem. Soc., Chem. Commun.*, (1992) 1560.
11 J. Weitkamp, R. Schumacher and U. Weiss, *Chem. Ing. Techn.*, 64 (1992) 1053.
12 A. Samoson and E. Lippmaa, *J. Magn. Reson.*, 84 (1989) 410.
13 D. Müller, *Ann. Phys. (Leipzig)*, 39 (1982) 451.
14 K.T. Mueller, J.M. Baltisberger, E.W. Wooten and A. Pines, *J. Phys. Chem.*, 96 (1992) 7001.
15 A.P.M. Kentgens, J.J.M. Lemmens, F.M.M. Geurts and W.S. Veeman, *J. Magn. Reson.*, 71 (1987) 62.
16 D. Massiot, C. Bessada, J.P. Coutures and F. Taulelle, *J. Magn. Reson.*, 90 (1990) 231.
17 W.J. Mortier, E. Van den Bossche and J.B. Uytterhoeven, *Zeolites*, 4 (1984) 41.

18 W.J. Mortier (Ed.), *Compilation of Extra Framework Sites in Zeolites*, Butterworth, Guildford, 1982, p. 26.
19 J.L. Lievens, J.P. Verduijn, A.-J. Bons and W.J. Mortier, *Zeolites*, 12 (1992) 699.
20 H. Koller, G. Engelhardt, A.P.M. Kentgens and J. Sauer, in preparation.
21 K.F.M.G.J. Scholle, Ph.D. thesis, University of Nijmegen, 1985.
22 J.J. Pluth, Ph.D. thesis, University of Washington, 1971, University Microfilms No. 71-28459.
23 P. Gallezot and B. Imelik, *C.R. Acad., Sc. Paris, Ser. B*, 271 (1970) 912.