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Characterisation of sodium cations in dehydrated zeolite NaX by ^{23}Na NMR spectroscopy

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Abstract

^{23}Na MAS, 2D nutation MAS, and DOR NMR spectroscopy has been applied to characterise the location of sodium cations in dehydrated zeolite NaX (Si/Al = 1.23). The ^{23}Na MAS NMR spectra recorded at three different magnetic field strengths were decomposed by computer simulation into five lines, which were attributed to five crystallographically distinct cation sites known from X-ray diffraction studies. The assignments of the lines follow from electric field gradient calculations at the ^{23}Na nuclei applying a simple point charge model based on crystal structure data. A weak Gaussian line at low field ($\delta_{iso} = -6$ ppm) is assigned to sodium cations at site I, two broad quadrupole patterns at the high-field side of the spectra are attributed to site I' ($\delta_{iso} = -19$ ppm, QCC = 5.2 MHz, $\eta = 0$) and site II cations ($\delta_{iso} = -15$ ppm, QCC = 4.6 MHz, $\eta = 0$), and two quadrupolar lines dominating the central region of the spectra originate from Na^+ at two different III' sites ($\delta_{iso} = -13$ and -29 ppm, QCC = 2.6 and 1.6 MHz, $\eta = 0.7$ and 0.9, respectively). Na^+ ions located on a second I' site could be identified from the DOR NMR spectra. The line assignment is further corroborated by the reasonable agreement of the site occupancies estimated from the line intensities with those determined by X-ray diffraction. In addition, sodium site populations of five dehydrated zeolites NaX and NaY with Si/Al ratios between 1.09 and 4.0 were derived from the ^{23}Na MAS NMR spectra.

Keywords: ^{23}Na double-rotation nuclear magnetic resonance; ^{23}Na magic-angle spinning nuclear magnetic resonance; Cation location; Nuclear quadrupole interaction; Solid-state nuclear magnetic resonance; Two-dimensional nutation ^{23}Na nuclear magnetic resonance; Zeolite NaX

1. Introduction

The understanding of the sorption, ion-exchange and catalytic properties of zeolites is strongly related to the knowledge of the location and distribution of the charge-compensating cations in the zeolite cavities and channels. The different crystallographic cation sites in faujasite-type X and Y zeolites as derived from X-ray and neutron diffraction studies are schematically depicted in Fig. 1 [1]. The populations of the different sites as a function of the Si/Al ratio have been described by a statistical thermodynamic model which agrees well with the results from diffraction experiments [2]. In dehydrated zeolites NaY (Si/Al > 2.4) the sodium cations are located

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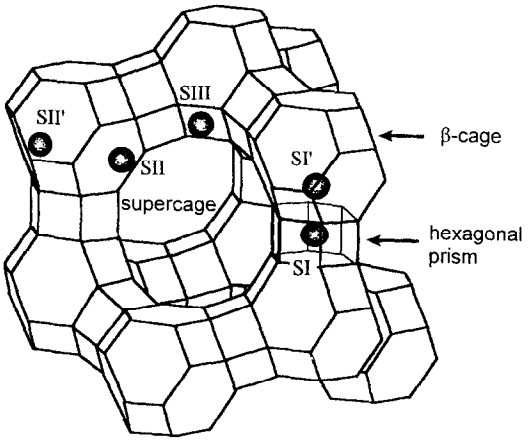


Fig. 1. Structure of the aluminosilicate framework of faujasites (zeolites X, Y) and the location of cation sites. The vertices of the framework are formed by Si and Al atoms joined by oxygen atoms, which are omitted for clarity.

on sites I′ and II near the centres of the six-ring windows in the β-cage and in the supercage, respectively, and (for Si/Al < 5) on sites I in the centre of the hexagonal prisms. In dehydrated zeolite NaX (Si/Al < 2), further cation locations near the idealised site III at the four rings in the supercage were found which are not occupied in NaY. In a recent single-crystal X-ray diffraction study of dehydrated zeolite NaX, Olson [3] succeeded in locating all sodium cations at sites I, I′, II and III′ and observed a splitting of the Na^+ ions in sites I′ and III′ between two and three closely related positions, respectively (not shown in Fig. 1).

Recent papers by several authors have shown that solid-state ^{23}Na NMR is a useful technique for characterising the location of sodium cations in zeolites NaY and related materials [4–9]. However, the correct interpretation of the spectra is still a matter of dispute. This is mainly because the quadrupole interactions of the ^{23}Na nuclei ($I = 3/2$) at the crystallographically distinct cation sites cause complex and heavily overlapping signal patterns in the ^{23}Na NMR spectra, which renders the separation of the resonances and their assignment difficult. To overcome these difficulties, it is essential (i) to apply an array of different NMR techniques including fast magic-angle spinning (MAS), double rotation (DOR), two-dimensional nutation with MAS and, most importantly, measurements at different magnetic field strengths; (ii) to study a number of NaY and NaX zeolite samples of different sodium contents (i.e., of different Si/Al ratios and/or degrees of cation exchange); and (iii) to compare the results for the cation distribution derived from the NMR spectra carefully with those obtained from reliable X-ray diffraction studies of related samples. In addition, electric field gradient calculations for the distinct sodium sites based on crystal structure data are particularly helpful in the simulation of the spectra and the line assignments. The general procedure for exploring cation siting in zeolites by ^{23}Na NMR spectroscopy has been summarised and exemplified for zeolite NaY in a recent paper [6].

In previous studies we have applied the above-mentioned methods to investigate cation siting in various dehydrated Y zeolites of type NaY [4,6], HNaY, BaNaY [4], LaNaY [7,8], CsNaY [10], and zeolite NaEMT [4]. In agreement with the cation locations known from XRD studies [1], three overlapping resonances have been resolved in the ^{23}Na MAS NMR spectrum of dehydrated zeolite NaY, a Gaussian line for Na^+ ions at site I (characterised by an isotropic chemical shift of $\delta_{iso} = -12$ ppm and a quadrupole coupling constant, QCC, close to zero), and two quadrupole powder patterns for sodium cations at sites I′ ($\delta_{iso} = -4$ ppm, QCC = 4.8 MHz) and II ($\delta_{iso} = -12$ ppm, QCC = 4.0 MHz) [6]. The populations of these sites were determined from the corrected [11] line intensities and agree well with those from XRD studies [2,12].

A different interpretation of the ^{23}Na MAS and DOR NMR spectra of dehydrated NaY has been presented by Verhulst et al. [5]. Although these authors assign the lines of sites I and II in the same way as given above, they attribute the resonance with $\delta_{iso} = -2$ ppm and QCC = 4.7 MHz to sodium cations at site III, and a further resonance with $\delta_{iso} = -19$ ppm and QCC = 2.3 MHz to sites I′ and II′. However, this interpretation seems questionable for the following reasons. (i) It is well known from X-ray diffraction studies (see, e.g., [12]) and theoretical considerations [2] that sites III and II′ are not occupied by sodium cations in dehydrated zeolite NaY. (ii) Electric field gradient calculations yield QCCs of 1.6–2.4 MHz for site III (in agreement with the experimental results for Na^+ on site III′ in zeolite NaX, see below) and 4.8 MHz for site I′ [6],

i.e., site III cations (if present at all) will not "have the largest quadrupole interaction" as concluded by the authors. (iii) The occupancy of site I′ by 8.6 Na/uc (Na atoms per unit cell) is too small compared with the 18 Na/uc obtained from XRD [12]. Following these arguments, the line characterised by $\delta_{iso} = -2$ ppm and QCC = 4.7 MHz has to be attributed to site I′ and not to site III cations, as already shown in Ref. [6]. The remaining resonance, although treated as a quadrupolar line with QCC = 2.3 MHz in Ref. [5], resembles a Gaussian-like line shape located at about −30 ppm (see Fig. 4 of Ref. [5]) and may originate from rehydrated Na^+ ions, which have been shown to give a similar line [6].

Very recently, Seidel and Boddenberg [9] concluded from static and MAS ^{23}Na NMR studies of zeolites NaY and NaX at the single field of $B_0 = 9.4$ T that the technique is well suited to distinguish between Na^+ ions in cubic sites I and non-cubic I′, II, II′ or III sites, but argue that further resolution of the latter sites is hardly feasible. We will refer to these conclusions below. Other authors also reported on ^{23}Na MAS [13–15], DOR [14] and static 2D nutation [16] NMR studies of dehydrated zeolite NaY, but most of the spectra show poor resolution and no detailed quantitative evaluation of the site populations was carried out.

The present paper reports on detailed ^{23}Na NMR investigations of the cation locations in dehydrated zeolite NaX (Si/Al = 1.23). Computer simulations of the ^{23}Na MAS NMR spectra measured at three different magnetic field strengths, complemented by DOR and 2D nutation NMR experiments, reveal the presence of six distinct resonances which, according to model calculations of QCC and the specific line intensities, were assigned to sites I, II and two different sites I′ and III′. The evolution of the various resonances is studied for five additional sodium faujasites with Si/Al ratios of 1.09, 1.18, 2.11, 2.5, and 4.0.

2. Experimental

The zeolites used in this study were commercial products (NaX-1.23, Fluka; NaY-2.5, Union Carbide) or kindly provided from other laboratories (see Acknowledgements). The framework Si/Al ratios of the samples were determined by ^{29}Si MAS NMR and are given in the sample designation, e.g., NaX-1.23 means a dehydrated NaX zeolite of Si/Al = 1.23. For all zeolites, no extra-framework aluminium could be detected in the ^{27}Al MAS NMR spectra. Prior to the NMR measurements the samples were carefully dehydrated at 673 K in vacuum below 10^{-2} Pa and filled into the NMR rotors under dry nitrogen gas in a glove box. The ^{23}Na MAS NMR experiments were carried out at Larmor frequencies of 105.8, 132.3 and 158.7 MHz on Bruker MSL-400, AMX-500 and AMX-600 spectrometers. Standard 4 mm double bearing Bruker MAS probes were used with spinning rates between 11 and 14 kHz. Single pulse excitation with 0.7 μs pulse width (corresponding $\pi/8$ flip angle) and 0.5 s pulse delay was applied. The DOR NMR spectra were measured at 105.8 MHz with spinning rates of the outer rotor of 1250, 1400 and 1500 Hz. Odd numbered DOR sidebands were suppressed by rotor-synchronised pulse excitation [17]. 2D nutation MAS experiments were carried out as described in Ref. [8]. The ^{23}Na NMR chemical shifts were referred to solid NaCl as external standard. Computer simulations of the ^{23}Na MAS NMR spectra were performed with the PC programs WINFIT of the Bruker WINMR software package and QUASAR (J.P. Amoureux et al., Lille, France). Simulations of the DOR NMR spectra were carried out by using the program QNMR (supplied by A. Samoson, Tallinn, Estonia). For the field gradient calculations a point charge model was applied [18] using the atomic positions from XRD studies and an oxygen charge of $-0.8\,e$.

3. Results and discussion

3.1. Zeolite NaX-1.23

3.1.1. ^{23}Na MAS NMR

As mentioned in Section 1, the XRD of zeolite NaX revealed Na^+ ions on sites I, I′, II, and III′, whereby site I′ is split into two and site III′ into three closely related positions [3]. Therefore, as many as seven resonances may appear in the ^{23}Na MAS NMR spectrum provided that all signals can be resolved. Applying the point charge model described in Ref. [18] and using the atomic coordinates given

Table 1
QCC and η of the sodium cation sites in zeolite NaX calculated by the point charge model and derived from the MAS NMR spectra

Site	Point charge model		Experiment	
	QCC/MHz	η	QCC/MHz	η
SI	0.2	0	0	0
SI′(1)	5.2	0	5.2	0
SI′(2)	3.6	0	3.6 [a]	0
SII	4.4	0	4.6	0
SIII′(1)	2.5	0.6	2.6	0.7
SIII′(2)	2.5	0.6	2.6	0.7
SIII′(3)	2.2	0.7	1.6	0.9

[a] from DOR simulation.

in [3] and oxygen net charges of $-0.8\ e$, QCC and η for all seven cation sites have been calculated. The results are summarised in Table 1.

The ^{23}Na MAS NMR spectra of the dehydrated zeolite NaX-1.23 measured at three different Larmor frequencies are shown in Fig. 2. The consistent simulation of the three spectra requires five components, three of which are similar to those observed in zeolite NaY [6] (see also below). The weak Gaussian line at lowest field exhibits no field-dependent shift ($\delta_{iso} = -6$ ppm) and is attributed to the sodium cations at site I. These Na^+ ions show a nearly perfect octahedral oxygen coordination and, therefore, no or only very small quadrupole interactions. The high-field range is characterised by two quadrupolar patterns which narrow and shift to lower field with increasing Larmor frequency. In analogy to NaY and in agreement with the field gradient calculations (see Table 1), the pattern with $\delta_{iso} = -19$ ppm and QCC = 5.2 MHz is attributed to the sodium cations at site I′(1) and that with $\delta_{iso} = -15$ ppm and QCC = 4.6 MHz to the cations at site II. The resonance of the second I′(2) sodium site detected by XRD [3] could not be separated in the MAS NMR spectrum. However, it will be shown below that both I′ sites can be resolved in the DOR spectrum. The central region of the spectra is very different from that observed for NaY and is dominated by two overlapping quadrupolar components simulated by $\delta_{iso} = -13$ ppm, QCC = 2.6 MHz, $\eta = 0.7$ and by $\delta_{iso} = -29$ ppm, QCC = 1.6 MHz, $\eta = 0.9$, respectively. As these two resonances do not appear in zeolite NaY and exhibit QCC and η close to those calculated for Na^+ ions on sites III′ (Table 1), they are ascribed to sodium cations at two different III′ sites. This assignment is corroborated by the crystal structure data [3] which revealed two III′ positions with similar oxygen environments (Na6 and Na6′ in [3]) and a third one in a different but more symmetrical environment (Na5). Obviously, the two former III′ positions cannot be resolved in the ^{23}Na MAS NMR spectrum.

The 105.8 MHz ^{23}Na MAS NMR spectrum of dehydrated zeolite NaX published by Seidel and

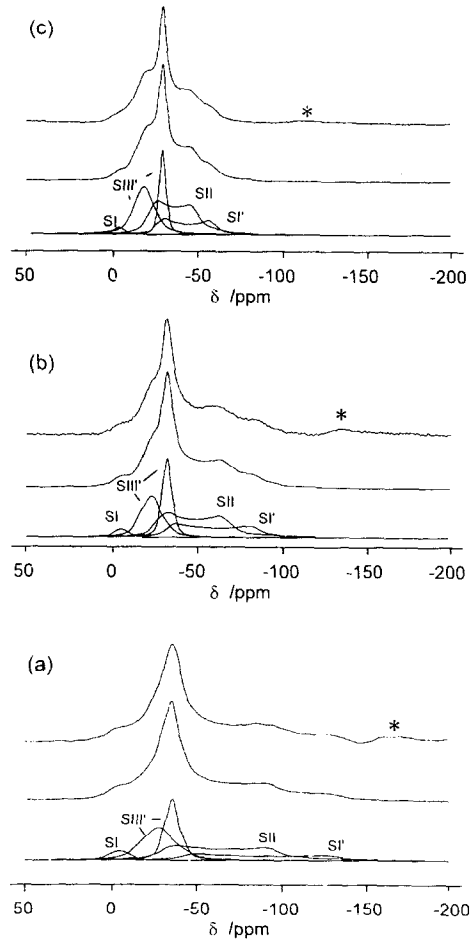


Fig. 2. Experimental and simulated ^{23}Na MAS NMR spectra of dehydrated zeolite NaX-1.23 measured at different Larmor frequencies: (a) 105.8 MHz, (b) 132.3 MHz, (c) 158.7 MHz. The experimental spectrum is shown in the upper trace, the simulated spectrum in the middle, and the components of the simulation at the bottom of (a), (b) and (c). The star denotes spinning sidebands.

Boddenberg [9] is similar to that shown at the bottom of Fig. 2, but has been considered by these authors to consist of only three lines, a single quadrupole pattern ascribed to Na^+ ions at sites II and I', and two Gaussian lines. The low-field line has been attributed to site I and the narrow central line to "non-localised cations escaping detection by the XRD method" showing motional averaging due to complexation with residual water molecules. Considering the recent XRD study of dehydrated NaX zeolite in which all sodium cations were located on distinct crystallographic sites [3] and the results of the field-dependent ^{23}Na MAS NMR studies discussed above, this interpretation must be reconsidered. It is obvious from the spectra shown in Fig. 2 (in particular from those measured at the high Larmor frequencies) that distinct shoulders appear at the high- and the low-field side of the spectra which indicate clearly the presence of two different quadrupolar patterns for sites I' and II, and of a second site III' line on the left side of the strong central resonance. Moreover, the clearly visible narrowing and shift to low field of the central line with increasing Larmor frequency prove unambiguously the quadrupolar nature of this line. In fact, the position of the line maximum measured at five spectrometer frequencies ν_0 between 52.9 and 156.7 MHz follow the expected $1/\nu_0^2$ dependence, and a QCC of 2.4 MHz has been estimated from the shifts, which agrees well with the result from the simulation. Note further that at least our sample does not contain water molecules (as shown by ^1H MAS NMR) for complexation and mobilisation of the cations, and that partial rehydration of dehydrated zeolite NaX causes a new resonance at about -20 ppm for hydrated Na^+ ions, quite different from the strong central line of the dehydrated sample.

The populations of the various sites by Na^+ ions were estimated from the line intensities of the simulated spectra obtained by the program QUASAR. This program includes the calculation of intensity contributions from possible excitations of satellite transitions and from spinning sidebands, and therefore provides true intensities of the different components without further corrections. However, errors of $\approx \pm 10\%$ in the calculated site populations may arise due to uncertainties introduced by the simulation and the procedure of fitting the spectra. The populations of sites I, I', II, III'(1,2) and III'(3) amount to 2, 21, 29, 22, and 12 Na/uc, respectively. These populations agree well with those obtained in a recent single crystal XRD study [3(0.5), 29(1.9), 31(0.3), 19(1.0), and 11(1.0) Na/uc, respectively; e.s.d.'s in parentheses] of a dehydrated zeolite NaX-1.18 with a slightly higher sodium content [3].

3.1.2. ^{23}Na 2D nutation MAS NMR

Two-dimensional quadrupole nutation NMR is a useful technique to separate resonances characterised by different quadrupole interactions, and has been applied previously to investigate sodium cations in NaY and LaNaY zeolites [4,8,16,19]. In the 2D nutation MAS NMR spectrum, the normal 1D MAS NMR spectrum is observed in the F2 dimension, and in the second dimension F1 the line positions depend on the strengths of their quadrupole interaction. If ν_{rf} symbolises the irradiated RF field amplitude, then for ^{23}Na, with $I = 3/2$, lines with strong quadrupole interactions (i.e., $\nu_Q = QCC/2 \gg \nu_{rf}$) appear in F1 at $2\nu_{rf}$, and those with small or vanishing QCC (i.e., $QCC/2 \ll \nu_{rf}$) at $1\nu_{rf}$. Intermediate quadrupole couplings give rise to broad and complex line shapes between $1\nu_{rf}$ and $2\nu_{rf}$ [20,21].

Fig. 3 shows the ^{23}Na 2D nutation MAS NMR spectrum of NaX-1.23. In agreement with the results derived from simulation of the MAS spectra, a weak line appears for site I cations ($QCC \cong 0$) at $1\nu_{rf}$ in F1 and -7 ppm in F2, and a broad line for sites I' and II ($QCC = 5.2$ and 4.6 MHz) at $2\nu_{rf}$ in F1, extending from about -40 to -100 ppm in F2. Although some fine structure of this resonance is visible, the two quadrupolar line shapes for sites I' and II cannot be clearly separated in F2. Centred at

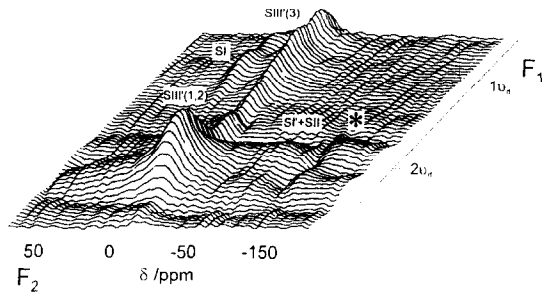


Fig. 3. ^{23}Na 2D nutation MAS NMR spectrum (105.8 MHz) of dehydrated zeolite NaX-1.23. The star denotes spinning sidebands.

about −36 ppm in F2, a complex line shape appears in the F1 direction which has to be ascribed to sodium cations at the III′ sites. The large intensity at $2\nu_{rf}$ is attributed to site III′(1,2) cations involved in large quadrupole interactions (QCC = 2.6 MHz), and the intensity appearing in the range between $2\nu_{rf}$ and $1\nu_{rf}$ indicates the presence of site III′(3) cations with smaller QCCs. The broad distribution of intensity in F1 may be explained by the results of theoretical calculations [21] which have shown that, in cases of large and intermediate quadrupole couplings, the MAS nutation spectrum is "smeared" and shifted to lower frequency compared with the static spectrum. On the other hand, the resolution in the F2 dimension is greatly improved by the application of MAS.

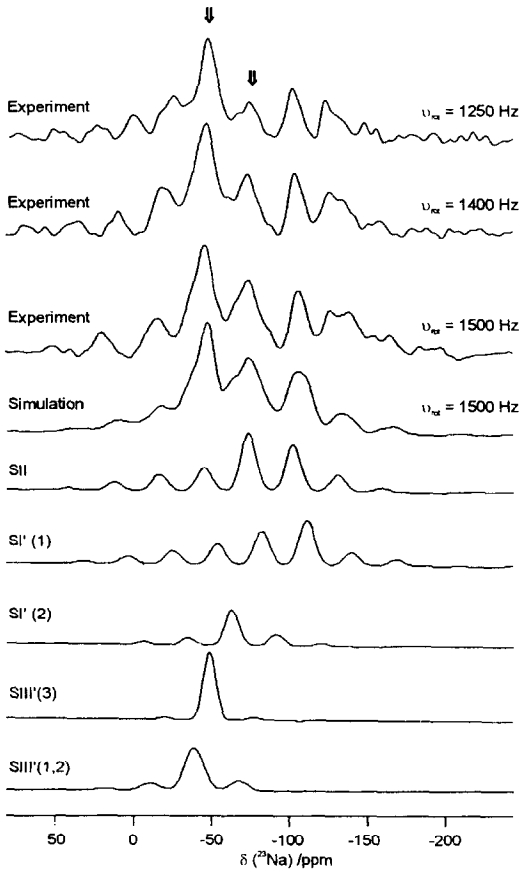


Fig. 4. ^{23}Na DOR NMR spectra (105.8 MHz) of dehydrated zeolite NaX-1.23 at three spinning frequencies of the outer rotor ν_{rot}, and simulation of the spectrum with ν_{rot} = 1500 Hz.

Table 2
^{23}Na NMR data and site populations (Na/uc) of dehydrated zeolites NaX-1.09, NaX-1.18, NaX-1.23, NaY-2.11, NaY-2.5, and NaY-4.0 as derived from ^{23}Na MAS NMR spectra

	▶SI	SI′	SII	SIII′(1,2)	SIII′(3)
NaX-1.09					
δ_{iso}/ppm		−19	−15	−14	−27
QCC/MHz		6.0	5.0	2.3	1.5
η		0	0	0.5	0.9
Na/uc	0	24	28	24	15
NaY-1.18					
δ_{iso}/ppm	−4	−19	−16	−14	−30
QCC/MHz	0	5.6	4.7	2.4	1.5
η	0	0	0	0.7	0.8
Na/uc	4	24	29	18	13
NaX-1.23					
δ_{iso}/ppm	−6	−19	−15	−13	−29
QCC/MHz	0	5.2	4.6	2.6	1.6
η	0	0	0	0.7	0.9
Na/uc	2	21	29	22	12
NaY-2.11					
δ_{iso}/ppm	−14	−5	−12		−16
QCC/MHz	0	4.9	4.0		2.2
η	0	0	0		0.6
Na/uc	4	20	31		7
NaY-2.5					
δ_{iso}/ppm	−12	−4	−12		
QCC/MHz	0	4.8	3.9		
η	0	0	0		
Na/uc	7	18	29		0
NaY-4.0					
δ_{iso}/ppm	−13	−3	−12		
QCC/MHz	0	4.8	3.9		
η	0	0.1	0.2		
Na/uc	2	8	29		0

Altogether, the 2D nutation MAS NMR spectrum of dehydrated zeolite NaX confirms, at least qualitatively, the simulation of the MAS NMR spectra by five resonances involved in different quadrupole interactions.

3.1.3. ^{23}Na DOR NMR

The 105.8 MHz ^{23}Na DOR NMR spectra of dehydrated zeolite NaX-1.23 registered with spinning rates of the outer rotor of 1250, 1400 and 1500 Hz are shown in the upper part of Fig. 4. The spectra

Table 3
^{23}Na NMR data and site populations (Na/uc) of zeolite NaX-1.23 as derived from ^{23}Na DOR NMR

	δ_{iso} /ppm	QCC/MHz	η	Na/uc
SI	–	–	–	–
SI'(1)	−20	5.0	0	25
SI'(2)	−28	3.6	0	8
SII	−18	4.5	0.1	30
SIII'(1,2)	−11	3.0	0.5	13
SIII'(3)	−31	1.9	0.9	10

exhibit two central lines (marked by arrows in Fig. 4) composed of several overlapping resonances and numerous spinning sidebands which can clearly be identified by the observed shifts at different spinning rates. Superimposition of the spinning sideband patterns and the central lines renders the interpretation of the DOR spectra difficult [22]. However, all details of the DOR spectrum can be reproduced by computer simulation using five components (see Fig. 4, lower part). The four component spectra of sites I'(1), II, III'(1,2) and III'(3) were calculated applying δ_{iso}, QCC and η derived from the MAS NMR spectra as starting parameters (see Table 2), and a further resonance (assuming QCC = 3.6 MHz and $\eta = 0$, see Table 1) for site I'(2) was added. The weak resonance of the cations on site I overlaps with spinning sidebands and cannot be clearly identified. The NMR parameters and site populations derived from the simulation of the DOR spectrum are summarised in Table 3. Comparison with the data in Table 2 reveals good agreement of the results from MAS and DOR for sites I'(1), II, III'(1,2) and III'(3).

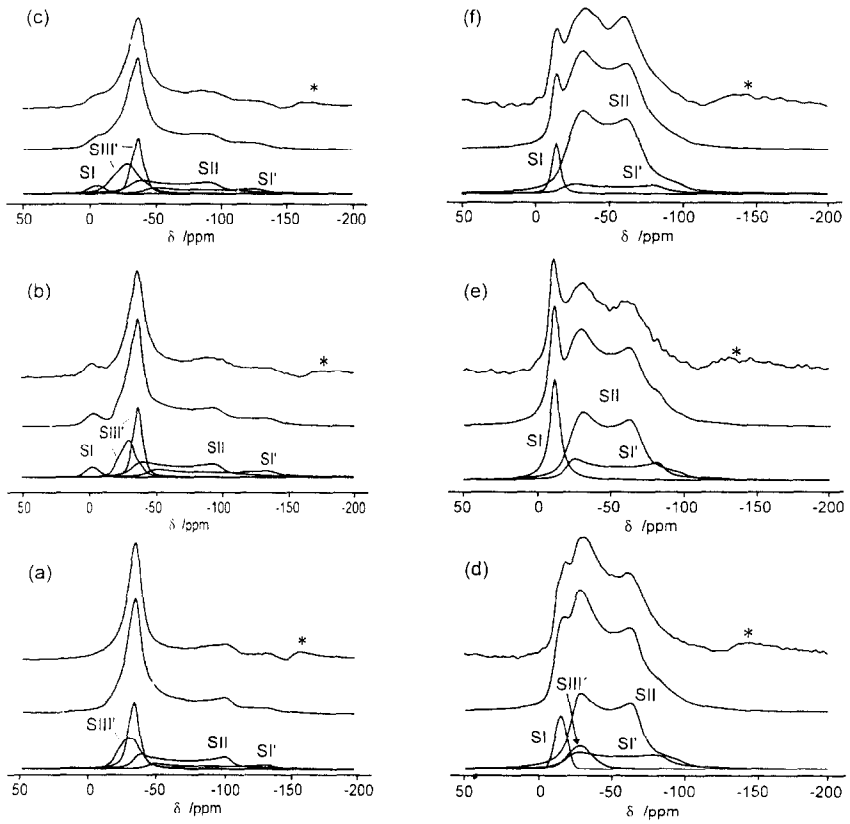


Fig. 5. Experimental and simulated ^{23}Na MAS NMR spectra (105.8 MHz) of dehydrated zeolites NaX and NaY with Si/Al ratios between 1.09 and 4.0: (a) NaX-1.09, (b) NaX-1.18, (c) NaX-1.23, (d) NaY-2.11, (e) NaY-2.5, (f) NaY-4.0. The experimental spectrum is shown in the upper trace, the simulated spectrum in the middle, and the components of the simulation at the bottom of (a)–(f). The star denotes spinning sidebands.

The higher population of site III'(1,2) derived from the MAS spectrum may be explained by overlapping of the corresponding resonance line with that of site I'(2), which could not be resolved in the MAS spectrum (see above).

3.2. Zeolites NaX and NaY with varying Si / Al ratio

To characterise the systematic changes of the site occupancies in dependence on the Si/Al ratio, the 105.8 MHz ^{23}Na MAS NMR spectra of four dehydrated sodium faujasites with Si/Al = 1.09, 1.18, 2.11, and 4.0 have also been measured, and are depicted in Fig. 5. For comparison, the spectra of NaY-2.5 [6] and NaX-1.23 (see above) are also shown. The corresponding NMR data (δ_{iso}, QCC, η) and site occupancies (Na/uc) obtained from the simulations are collected in Table 2.

Examination of Table 2 shows that the QCC of sites I' and II increases with decreasing Si/Al ratio of the faujasite samples. This observation is explained by the stronger electrostatic repulsion of the Na^+ ions with increasing number of cations in the zeolite, resulting in shorter distances between the sodium cations and the coordinating oxygen atoms of the six-ring windows. Electric field gradient calculations by the point charge model [18] confirm the increase in QCC with decreasing Na–O distances.

In Fig. 6, the population factors P_{Na} (i.e., the site occupancies Na/uc divided by the crystallographic multiplicity of the distinct positions, which is 16 for site I, 32 for sites I' and II, and 96 for site III) of the different sites are plotted against the number of aluminium atoms per unit cell (which is equivalent to Na/uc since Al/Na = 1). For comparison, the population factors determined from XRD studies of zeolites NaY-2.4 [12] and NaX-1.18 [3] are also included (open symbols). In general, the populations derived from the ^{23}Na MAS NMR spectra follow the expected trends [2]. With increasing numbers of Al atoms per unit cell the Na^+ populations of sites I', II and III increase continuously, while the occupancy of site I passes a maximum at about 50–60 Al/uc and decreases at higher Al contents. Above ≈ 40 Al/uc essentially all site II locations are occupied by Na^+, but site I' occupancies remain slightly below the maximum value even at high numbers of Al per unit cell. Irrespective of the total cation content, only

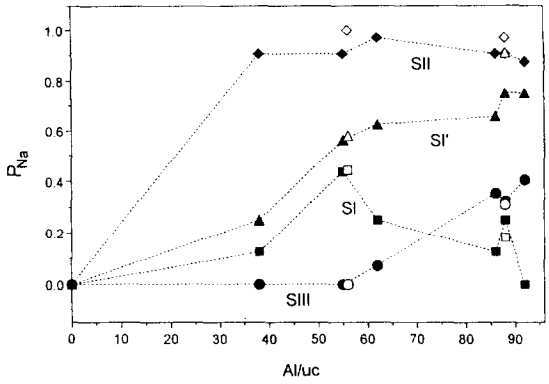


Fig. 6. Population factors P_{Na} of cation sites in zeolites NaX and NaY as a function of the number of Al atoms per unit cell. The results of this study are represented by filled symbols connected by dashed lines: ■, site I; ▲, site I'; ◆, site II; ●, site III. The corresponding open symbols represent XRD results for NaY-2.4 [12] and NaX-1.18 [3].

up to ≈ 40% of the available site I and site III locations are occupied by Na^+ ions.

In summary, NMR spectroscopy is a useful complement to diffraction methods and may profitably be applied to study the cation locations in homologous series of, e.g., cation-exchanged, thermally treated, partially rehydrated or sorbate-loaded zeolites, which appears to be rather time-consuming and cumbersome by diffraction techniques. In addition, NMR observes, in principle, all cations present in the zeolite, whereas a certain fraction of them often escapes detection by X-ray diffraction. This is particularly true in powder XRD studies of microcrystalline zeolites, which are the materials usually available.

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