SELECTIVE AND NON-SELECTIVE NMR EXCITATION OF QUADRUPOLAR NUCLEI IN THE SOLID STATE

Pascal P. MAN a, Jacek KLINOWSKI a, Arlette TROKINER b, Hélène ZANNI b and Pierre PAPON b

a Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, UK
b Laboratoire de Physique Thérmique, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 5, France

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Spectral intensities of quadrupolar nuclei and the radiofrequency (rf) pulse lengths for selective and non-selective excitation of any single-quantum NMR transition in the solid state are calculated. When nuclei of the same element occupy sites which experience different electric field gradients, the spectra are quantitatively reliable only when the length of the rf pulse is much smaller than \( \frac{1}{2} \omega_{Q} (\frac{1}{2} I + 1) - m(I+m+1) \). By using hydrated samples and short rf pulses, quantitative determination of aluminium by \(^{27}\)Al NMR in thermally treated (ultrastable) zeolite Y has been achieved. Quadrupole nutation NMR reveals novel information about the various aluminium species present.

1. Introduction

The quantitative determination of the quadrupolar \((I>1/2)\) spin populations in powdered samples is a major concern in NMR. The energy levels are shifted by the quadrupolar interaction, and for half-integer spins only the central transition \((+1/2 \rightarrow -1/2)\) is normally detected (as opposed to excited), which affects the optimal excitation conditions. In general, in the presence of the quadrupole interaction the \(\pi/2\) pulse is shorter than for a spin 1/2 nucleus with the same gyromagnetic ratio, \(\gamma\), and line intensities of the individual transitions are smaller and decrease with increasing \(I\). All the energy levels are strongly perturbed by the pulse when the strength of the first-order quadrupolar interaction \(\omega_{Q}\) (see eq. (2) below) is much smaller than the strength of the pulse, \(\omega_{\text{rf}}\), related to the amplitude of the rf magnetic field, \(B_{1}\), by \(\omega_{\text{rf}}=\gamma B_{1}\). In this case, the excitation is non-selective, and the pulse length \(t_{\text{RF}}\) which maximizes the line intensity is \(t_{\text{RF}}=\pi/2\). For \(\omega_{Q} \gg \omega_{\text{rf}}\) only the two neighbouring energy levels which are irradiated on resonance are strongly perturbed; others are only weakly affected and the excitation is therefore selective. In the selective excitation of the central line, maximum line intensity is achieved [1] by pulses whose lengths fulfil the condition \(t_{\text{RF}}(I+1/2)\omega_{\text{rf}}=\pi/2\). Schmidt [2] established the selective excitation conditions for single quantum transitions. Unfortunately, his lecture notes are not easily accessible and the main result, the table relating pulse length and line intensity, is often quoted [3] without any hint of how it was derived. As a result, it is often incorrectly assumed that if the pulse length is \(1/(1+1/2)\) of that for a \(\pi/2\) pulse length determined in solution, only the central transition is excited [4,5]. The important chemical consequence of this is that NMR spectral intensities are often incompatible with the results of the elemental chemical analysis of the sample [6]. One important case concerns the \(^{27}\)Al NMR spectra of zeolites. As a result of very strong quadrupole interactions some extra-framework aluminium in thermally treated zeolites is "invisible" to conventional NMR [7]. We examine the conditions required for the quantitative determination of the concentration and chemical environment of quadrupolar nuclei in solids, and demonstrate that in fact all aluminium in zeolites can be observed.

For short rf pulses the observed intensity of the central transition is independent of \(\omega_{Q}\) [8]. Central line intensities of a spin \(I=5/2\) for a large range of \(\omega_{Q}\) have been calculated [9]; so has the effect of pulse length upon line intensity [10,11] for \(I=3/2\) and...
any pair of values \((\omega_Q, \omega_{rf})\). The two extreme cases
\((\omega_Q \ll \omega_{rf} \text{ and } \omega_Q \gg \omega_{rf})\) were experimentally illus-
trated with the \(^{23}\text{Na} \ (I=3/2)\) spectra in a mixture of powdered NaCl and NaNO\(_2\) \([8,10]\).

2. Theory

In the rotating frame the Hamiltonian, \(H\), expressed in angular frequency units, of a quadrupolar
spin \(I\) in a strong static magnetic field and an rf magnetic field is

\[
H = H_Q^{(1)} + H_A - \omega_{rf} I_z,
\]

with

\[
H_Q^{(1)} = \frac{1}{2} \omega_Q \left[ 3I_z^2 - I(I+1) \right]
\]

and

\[
H_A = -\omega_Q (1 + 2n) I_z,
\]

where \(\omega_{rf}\) is the coupling of the spin with the rf
magnetic field \(B_{rf}\), \(H_Q^{(1)}\) is the first-order quadrupole
interaction and \(H_A\) is the frequency shift required to
irradiate the transition \((n+1, n)\) on resonance. For the
central transition \((n=-1/2)\), \(H_d=0\). \(\omega_Q\) is a
function of \(I\), the quadrupolar coupling constant
\(e^2Q/h\), the asymmetry parameter, \(\eta\), and the Euler
angles describing the orientation of the EFG.

In continuous wave (cw) NMR the line intensity
is proportional to the spin population. The line inten-
sity \(F_{cw}^{m+1,m}\) and the relative line intensity,
\(I_{cw}^{m+1,m}\) corresponding to the transition \((m+1, m)\)
are proportional to the square of the time-dependent
perturbation between the states \(|m+1\rangle\) and \(|m\rangle\).
The perturbation is the coupling of the spins to
the rf magnetic field. In the laboratory frame, this
perturbation is time dependent. We have

\[
F_{cw}^{m+1,m} \propto |\langle m+1 | I_z | m \rangle|^2 \xi^2,
\]

with

\[
\xi(m+1, m) = \sqrt{I(I+1) - m(m+1)},
\]

\[
I_{cw}^{m+1,m} \propto \xi^2 / \sum_{m=-i}^{I-1} \xi^2.
\]

In pulsed NMR the line intensity and the initial
value of the free induction decay \(F(t_p)\) are propor-
tional to the spin population. Line intensity is also
related to the density matrix \(\rho(t_p)\) at the end of the
pulse by

\[
\sum_{m=-i}^{I-1} F(t_p) = \text{Tr}[\rho(t_p) I_z],
\]

\[
\rho(t_p) = \exp(-iH_{rf}t_p) I_z \exp(iH_{rf}t_p),
\]

where \(\text{Tr}\) denotes a trace.

In the case of non-selective (NS) excitation, \(H_Q^{(1)}\) and \(H_d\) in eq. (1) are negligible. Eq. (8) then
becomes

\[
\rho(t_p) = I_z \cos(\omega_{rf}t_p) + I_x \sin(\omega_{rf}t_p).
\]

The submatrix \(A\) of \(I_z\) expressed in the base \(|m+1\rangle, \n
\]

\[
A = \begin{pmatrix}
0 & -\frac{1}{2} i \xi^2 \\
\frac{1}{2} i \xi^2 & 0
\end{pmatrix}.
\]

It follows that the line intensity \(F_{NS}^{m+1,m}(t_p)\) and the
relative line intensity \(I_{NS}^{m+1,m}(t_p)\), normalized as
described in eq. (6), are

\[
F_{NS}^{m+1,m}(t_p) = \frac{1}{2} \xi^2 \sin(\omega_{rf}t_p),
\]

\[
I_{NS}^{m+1,m}(t_p) = \xi^2 \sin(\omega_{rf}t_p)/2 \sum_{m=-i}^{I-1} \xi^2.
\]

Eqs. (6) and (12) reveal that \(I_{NS}^{m+1,m}(t_p)\) and \(I_{cw}^{m+1,m}\) are proportional to each other. It follows that
pulsed and cw NMR are equivalent when \(\omega_Q \ll \omega_{rf}\).

In the case of selective (S) excitation all terms in
eq. (1) must be taken into account. However, we can
now neglect the effects of the pulse on all the trans-
itions apart from those corresponding to the on-res-
onance frequency. The contribution to the line
intensity is \(F_{S}^{m+1,m}(t_p)\) corresponding to the irra-
diated transition \((m+1, m)\) \((n=m\) in eq. (3)). The
matrix \(B\) of \(H\) in the base \(|m+1\rangle, |m\rangle\) is

\[
B = -\omega_Q [m^2 + m + \frac{1}{2}(I(I+1))] I + C,
\]

where \(I\) is the identity matrix and

\[
C = \begin{pmatrix}
0 & -\frac{1}{2} \omega_{rf} \xi \\
-\frac{1}{2} \omega_{rf} \xi & 0
\end{pmatrix}.
\]

The identity operator or the identity matrix do not
contribute to the signal. \(H_Q^{(1)}\) and \(H_d\) do not appear
explicitly in the computation. Only \(C\), the matrix of
the rf pulse in the base \(|m+1\rangle, |m\rangle\) remains in
eq. (13). The main effect of a strong quadrupolar

interaction is to split the energy levels in such a way that only the two levels associated with on-resonance frequency are strongly perturbed. Since the equations do not depend on \( \omega_0 \), the results are formally valid for single crystals as well as powdered samples. However, in practice it is difficult to achieve selective excitation for non-central transitions in powders.

The matrix \( \mathbf{C} \) can be easily diagonalized, so that the density matrix becomes

\[
p(t_p) = \frac{1}{2} \left( \begin{array}{cc} \cos(\omega_r \xi t_p) & -i \sin(\omega_r \xi t_p) \\ i \sin(\omega_r \xi t_p) & -\cos(\omega_r \xi t_p) \end{array} \right).
\] (15)

It follows that the line intensity \( I_{S}^{m+1,m}(t_p) \) and the relative line intensity \( I_{S}^{m+1,m}(t_p) \) of the on-resonance transition \((m+1, m)\) normalized as described by eq. (6) are

\[
I_{S}^{m+1,m}(t_p) = \frac{1}{2} \xi \sin(\omega_r \xi t_p),
\] (16)

\[
I_{S}^{m+1,m}(t_p) = \xi \sin(\omega_r \xi t_p)/2 \sum_{m=-1}^{l-1} \xi^2.
\] (17)

As explained above, \( F_{S}^{m+1,m}(t_0) \) and \( I_{S}^{m+1,m}(t_0) \) do not depend explicitly on the value of \( \omega_0 \) in the selective excitation condition \( (\omega_0 \gg \omega_q) \), but only on the pulse length, \( t_p \). By comparing eqs. (12) and (17), we see that for selective excitation the pulse length which maximizes the intensity of the on-resonance transition \((m+1, m)\) is \( \xi \) times shorter than that for the non-selective excitation which is usually defined as \( \omega_q t_p = \pi/2 \). Furthermore, there is also a loss of line intensity by a factor of \( \xi \). Table 1 gives the complete list of spectral intensities for both types of excitation [2]. Eqs. (12) and (17) represent the two extreme limits between which all line intensities for the intermediate case \( (\omega_0 \approx \omega_q) \) will be found.

If, however, the sample is monocristalline and the pulse length \( t_p \) is sufficiently small, so that

\[
\sin(\omega_r \xi t_p) \approx \omega_r \xi t_p,
\] (18)

eqs. (12) and (17) are identical:

\[
I_{S}^{m+1,m}(t_p) = \xi^2 \omega_q t_p/2 \sum_{m=-1}^{l-1} \xi^2,
\] (19)

where \( \xi \) has the largest value for the central transition. It follows that when eq. (18) is valid for the central transition, it is valid for other transition as well. The value of \( I_{S}^{m+1,m}(t_0) \) given by eq. (19) is directly proportional to \( t_p \). Consequently, there is a linear region for each \((m+1, m)\) transition, in which line intensity is independent of the strength of the quadrupolar interaction, if the transition is excited on resonance. Furthermore, \( I_{S}^{m+1,m}(t_0) \) is proportional to \( \xi^2 \), as is \( I_{S}^{m+1,m} \) given by eq. (6). It follows that for short enough pulses the relative line intensity of the transition excited on resonance is the same as in cw NMR. All the above calculations take into account only the first-order quadrupole interaction.

3. Experimental

\(^{29}\text{Si} \) and \(^{27}\text{Al} \) NMR spectra were obtained using a Bruker MSL-400 multinuclear spectrometer operating at 79.5 and 104.2 MHz, respectively. A homemade NMR probehead equipped with an Andrew-Beams rotor was used for the \(^{29}\text{Si} \) spectra. The samples were spun in air at about 2.5 kHz and \( \pi/4 \) radiofrequency pulses were applied with a 30 s recycle delay. The duration of the \( \pi/2 \) pulse was determined using the \(^{127}\text{I} \) resonance of an aqueous solution of potassium iodide. \(^{29}\text{Si} \) chemical shifts are given in ppm from external tetramethylsilane (TMS). 1500 free-induction decays (FIDs) were accumulated for each sample.

In order to avoid spinning sidebands which often coincide with genuine signals, the \(^{27}\text{Al} \) spectra were measured without MAS. Conventional spectra were obtained using a aluminium-free probehead containing 100 mg of sample. 5000 and 20000 FIDs were accumulated for pulse lengths of \( \pi/6 \) and \( \pi/20 \), respectively, with a recycle delay of 0.2 s and spectral width of 125 kHz. Instrumental deadtime was 12 \( \mu s \). The duration of the \( \pi/2 \) pulse (9 \( \mu s \)) and the \(^{27}\text{Al} \) chemical shifts were determined using an aqueous solution of Al(NO₃)₃.

Quadrupole nutation NMR \([8,10]\) can also provide new insights into the behaviour of \( l > 1/2 \) nuclei in solids. In this technique, a series of free-induction decays during the interval \( t_2 \) is acquired using powerful resonant radiofrequency pulses while monotonically increasing the length, \( t_0 \), of the pulse. Double Fourier transformation in \( t_2 \) and \( t_0 \) gives a two-dimensional (2D) NMR spectrum with the axes \( F_2 \) (containing combined chemical shift and the second-order quadrupole shift) and \( F_1 \) (containing quadrupolar information only). The technique per-
Table 1
Intensities and pulse lengths for selective excitation of single quantum transitions in pulsed NMR and line intensity in cw NMR for a single crystal. For a powdered sample, only the central transition measurements obtained with short rf pulses are useful.

<table>
<thead>
<tr>
<th>$I$</th>
<th>Transition</th>
<th>$\xi^2$</th>
<th>$1/\Sigma \xi^2$</th>
<th>$90^\circ$ pulse length $1/\xi$</th>
<th>line intensity $\xi/\Sigma \xi^2$</th>
<th>cw or NS excitation or short rf pulse $^a$ $\xi/\Sigma \xi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>$1/2\leftrightarrow 1/2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>all</td>
<td>$1/4$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$\pm 1\leftrightarrow 0$</td>
<td>2</td>
<td>$1/\sqrt{2}=0.707$</td>
<td>$\sqrt{2}/4=0.354$</td>
<td>2/4=0.500</td>
<td></td>
</tr>
<tr>
<td>3/2</td>
<td>all</td>
<td>$1/10$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$\pm 3/2\leftrightarrow 1/2$</td>
<td>3</td>
<td>$1/\sqrt{3}=0.578$</td>
<td>$\sqrt{3}/10=0.173$</td>
<td>3/10=0.300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1/2\leftrightarrow -1/2$</td>
<td>4</td>
<td>$1/\sqrt{4}=0.500$</td>
<td>$\sqrt{4}/10=0.200$</td>
<td>4/10=0.400</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>all</td>
<td>$1/35$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$\pm 5/2\leftrightarrow 3/2$</td>
<td>5</td>
<td>$1/\sqrt{5}=0.447$</td>
<td>$\sqrt{5}/35=0.064$</td>
<td>5/35=0.143</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm 3/2\leftrightarrow 1/2$</td>
<td>8</td>
<td>$1/\sqrt{8}=0.354$</td>
<td>$\sqrt{8}/35=0.081$</td>
<td>8/35=0.228</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1/2\leftrightarrow -1/2$</td>
<td>9</td>
<td>$1/\sqrt{9}=0.333$</td>
<td>$\sqrt{9}/35=0.086$</td>
<td>9/35=0.257</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>all</td>
<td>$1/56$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$\pm 3\leftrightarrow 2$</td>
<td>6</td>
<td>$1/\sqrt{6}=0.408$</td>
<td>$\sqrt{6}/56=0.044$</td>
<td>6/56=0.107</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm 2\leftrightarrow 1$</td>
<td>10</td>
<td>$1/\sqrt{10}=0.316$</td>
<td>$\sqrt{10}/56=0.057$</td>
<td>10/56=0.179</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm 1\leftrightarrow 0$</td>
<td>12</td>
<td>$1/\sqrt{12}=0.289$</td>
<td>$\sqrt{12}/56=0.062$</td>
<td>12/56=0.214</td>
<td></td>
</tr>
<tr>
<td>7/2</td>
<td>all</td>
<td>$1/84$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$\pm 7/2\leftrightarrow 5/2$</td>
<td>7</td>
<td>$1/\sqrt{7}=0.378$</td>
<td>$\sqrt{7}/84=0.031$</td>
<td>7/84=0.083</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm 5/2\leftrightarrow 3/2$</td>
<td>12</td>
<td>$1/\sqrt{12}=0.289$</td>
<td>$\sqrt{12}/84=0.041$</td>
<td>12/84=0.143</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm 3/2\leftrightarrow 1/2$</td>
<td>15</td>
<td>$1/\sqrt{15}=0.258$</td>
<td>$\sqrt{15}/84=0.046$</td>
<td>15/84=0.179</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1/2\leftrightarrow -1/2$</td>
<td>16</td>
<td>$1/\sqrt{16}=0.250$</td>
<td>$\sqrt{16}/84=0.048$</td>
<td>16/84=0.190</td>
<td></td>
</tr>
<tr>
<td>9/2</td>
<td>all</td>
<td>$1/165$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$\pm 9/2\leftrightarrow 7/2$</td>
<td>9</td>
<td>$1/\sqrt{9}=0.333$</td>
<td>$\sqrt{9}/165=0.018$</td>
<td>9/165=0.055</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm 7/2\leftrightarrow 5/2$</td>
<td>16</td>
<td>$1/\sqrt{16}=0.250$</td>
<td>$\sqrt{16}/165=0.024$</td>
<td>16/165=0.097</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm 5/2\leftrightarrow 3/2$</td>
<td>21</td>
<td>$1/\sqrt{21}=0.218$</td>
<td>$\sqrt{21}/165=0.028$</td>
<td>21/165=0.127</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm 3/2\leftrightarrow 1/2$</td>
<td>24</td>
<td>$1/\sqrt{24}=0.204$</td>
<td>$\sqrt{24}/165=0.030$</td>
<td>24/165=0.145</td>
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</tr>
<tr>
<td></td>
<td>$1/2\leftrightarrow -1/2$</td>
<td>25</td>
<td>$1/\sqrt{25}=0.200$</td>
<td>$\sqrt{25}/165=0.030$</td>
<td>25/165=0.152</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Useful for single crystal study only where each $(m+1, m)$ transition can be individually excited on resonance.
4, 5 and 6 were kept at 525°C for 0.25, 1, 2, 17 and 19 h, respectively, before being cooled down. Water was slowly injected into the tube by a peristaltic pump so that the partial pressure of H₂O above the sample was 1 atm [12]. The samples were finally hydrated in a desiccator with saturated NH₄NO₃, which is necessary for well-developed NMR signals to be observed [13-15]. During rehydration the protons of bridging hydroxyls coordinate to water and to NF Al to produce H₃O⁺ and Al(H₂O)₃⁺ complexes, respectively, thus restoring symmetry of the Al.

4. Results and discussion

Unit cell parameters of the samples are listed in table 2. It is clear that a₀ decreases with dealumination time, while the ²⁹Si MAS NMR spectra show that the framework Si/Al ratio increases with the duration of treatment. The spectra (fig. 1) were deconvoluted using Gaussian peak shapes. The framework (Si/Al)_{NMR} ratio and the number of NF aluminium atoms per unit cell Al_{Nf} were calculated using the formulae [7]

\[
(Si/Al)_{NMR} = \frac{I_2 + I_3 + I_0 + I_1}{I_4 + 0.75I_3 + 0.5I_2 + 0.25I_1}, \quad (20)
\]

\[
Al_{Nf} = 192 \frac{r-c}{(1+c)(1+r)}, \quad (21)
\]

where \(I_\alpha\) is the spectral intensity corresponding to the Si(nAl) structural unit, and c and r the framework Si/Al ratios before and after hydrothermal treatment, respectively. Eq. (21) assumes a perfect unit cell in which the number of ²⁷Al nuclei, but not that of ²⁹Si nuclei, is constant. The number of framework aluminium atoms per unit cell, Al_{f}, was determined

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating time (h)</th>
<th>XRD</th>
<th>²⁹Si MAS NMR</th>
<th>²⁷Al NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a₀(Å)</td>
<td>Al_f</td>
<td>Si/Al</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>24.71</td>
<td>51</td>
<td>2.53</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>24.60</td>
<td>39</td>
<td>4.00</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>24.59</td>
<td>38</td>
<td>3.91</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>24.60</td>
<td>39</td>
<td>4.43</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>24.51</td>
<td>29</td>
<td>5.33</td>
</tr>
<tr>
<td>5</td>
<td>17</td>
<td>24.47</td>
<td>25</td>
<td>6.02</td>
</tr>
<tr>
<td>6</td>
<td>19</td>
<td>24.45</td>
<td>23</td>
<td>6.19</td>
</tr>
</tbody>
</table>
using the relationship between $a_0$ (in Å) and $(\text{Si}/\text{Al})_{\text{NMR}}$ [16]:

$$a_1 = 170.1 \left( a_0 - 24.238 \right). \tag{22}$$

Static $^{27}\text{Al}$ NMR spectra obtained with $\pi/6$ pulses are given in fig. 2a, those with $\pi/20$ pulses in fig. 2b. The spectra are in the absolute intensity mode, relative to sample 0 in each series. Spectral intensity was obtained by integration from 500 to $-400$ ppm and is indicated in the right-hand column. It was corrected for the different water content of different samples, and therefore refers to the same number of Al atoms. Fig. 2a shows that the intensity in sample 1 is much lower than in sample 0, but remains approximately constant afterwards. The ratio of these two sets of line intensities is very close to the value of 1.50 calculated for the $F_{\text{NS}}/F_{\text{N}}$ from eqs. (11) and (16) and $\omega_{1/2} = \pi/6$. It is clear that while non-selective excitation takes place in the parent sample, quadrupolar effects in thermally treated samples are so much larger that only selective excitation is possible which, for a $\pi/6$ pulse, leads to a considerable reduction in spectral intensity. On the other hand, for $\omega_{1/2} = \pi/20$ eqs. (11) and (16) give $F_{\text{NS}}/F_{\text{N}} = 1.03$, and fig. 2b indeed shows that the intensities of all the spectra including that of the starting material are much more similar than for the $\pi/6$ pulse. For the very short pulses applied here, the difference in spectral intensity between selective and non-selective excitation should be only 3%. In practice, however, some spectral intensity is lost in the dead-time of the receiver. This is much more important for the treated samples 1–6, which give broad $^{27}\text{Al}$ lines, than for the starting material. Results from samples treated at 700°C instead of 525°C were very similar.

The question remains as to how to assign the various spectral features to aluminium in different

Fig. 2. Static $^{27}\text{Al}$ spectra on the absolute intensity scale acquired with (a) $\pi/6$; and (b) $\pi/20$ pulses. Numbers refer to the relative intensity of each spectrum corrected for water content.
chemical environments in the sample. The position of $^{27}$Al NMR signals in 2D spectra is described using two axes: $F_1$ (labelled in kHz) and $F_2$ (in ppm). The spectrum of the starting material (fig. 3a), which contains only one kind ($F$) of Al sites is composed of two signals at (70 kHz, 60 ppm) and (180 kHz, 60 ppm), both with the same linewidth in the $F_2$ dimension. The presence of the second signal in the sample containing only one kind of Al is due to the fact that the quadrupolar interaction characteristic of the framework Al and the strength of the rf pulse are of the same order of magnitude [17]. On the other hand, the spectrum of sample 1 (fig. 3b) consists of four peaks: at (70 kHz, 60 ppm), (70 kHz, -6 ppm), (203 kHz, 74 ppm) and (203 kHz, 3 ppm). As in fig. 3a, the first signal corresponds to framework Al, and the second to mobile Al species in octahedral environments. The positions of the other two (one relatively sharp and one very broad) clearly indicate that the associated Al is in a strongly asymmetric environment. This is because their frequency along the $F_1$ axis is almost exactly three times that for the first signal (for $I = 5/2$, $\zeta = 3$ and the excitation is selective). The 2D spectrum of sample 6 (fig. 3c) also consists of four signals: at (68 kHz, 60 ppm), (68 kHz, -10 ppm), (200 kHz, 79 ppm) and (200 kHz, 22 ppm). The signal corresponding to the framework Al peak has decreased in intensity in comparison with fig. 3b, because dealumination of sample 6 is more advanced. The sharp peak of the mobile Al has disappeared, but a broad NF octahedral Al peak remains. The third signal has also decreased in intensity in comparison with the fourth. The fourth signal must therefore correspond to NF aluminium. All signals apart from the third are detectable by conventional (one-dimensional) $^{27}$Al MAS NMR.

Assume that the lineshape and linewidth of NMR signals from framework Al in dealuminated samples is the same as in the starting material. Deconvolution of the $^{27}$Al spectra then gives the apparent relative amounts of NF aluminium, $A_{INF}$, listed in the last column of table 2. It is clear that these values are completely incompatible with the reliable information from $^{29}$Si NMR and XRD, both of which indicate the presence of much less NF aluminium. It is also clear from fig. 3c that the intensity of the signal at (68 kHz, 60 ppm) is insufficient to account for all the framework aluminium, which amounts to 50% of that in the parent sample. The only possible conclusion is that one of the two peaks located at 200 kHz along $F_1$ in the 2D spectra (figs. 3b and 3c) represents Al in tetrahedra distorted following the hydrothermal treatment, possibly resulting in the formation of AlOH groups. Ray et al. [18] found that while $^{29}$Si NMR and XRD indicate dealumi-
nation of the zeolite framework, $^{27}$Al MAS NMR does not detect any decrease in the amount of tetrahedral aluminium. The reason is that signals corresponding to the same nuclear species in environments of different electric field gradient often overlap in conventional NMR spectra as a result of the shifting of the line position by the second-order quadrupole interaction.

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References