Sensitivity enhancements in MQ-MAS NMR of spin-5/2 nuclei using modulated *rf* mixing pulses [1]

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Abstract

An X–$\overline{\text{X}}$ pulse train with stepped modulation frequency was employed to enhance the multiple-quantum to single-quantum coherence transfer in the mixing period of the multiple-quantum magic-angle spinning (MQ-MAS) experiment for spin $I = 5/2$ nuclei. Two MQ-MAS pulse sequences employing this mixing scheme for the triple-to-single and quintuple-to-single quantum coherence transfers have been designed and their performance is demonstrated for ^{27}Al on samples of $NaSi_3AlO_8$ and $9Al_2O_3 \cdot 2B_2O_3$. Compared to the standard single-pulse mixing sequences, the sensitivity is approximately doubled in the present experiments. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Since the introduction of multiple-quantum magic-angle spinning (MQ-MAS) [1], a number of research groups have focused on improving the sensitivity of the MQ-MAS experiment [2–12], which generally suffers from the low coherence transfer amplitudes between multiple (MQ) and single (1Q) quantum coherences [13]. While most researchers focused on optimizing the MQ coherence preparation [2–10], recent studies have found that significant sensitivity enhancements can be obtained using modified triple quantum (3Q) → single quantum (1Q)

mixing schemes [3,10–12]. Given that the majority of these proposed improvements have, to date, only been demonstrated for spin $I = 3/2$ nuclei [3,5–9,11,12] we have investigated the possible advantages of employing an X–$\overline{\text{X}}$ pulse train for MQ → 1Q mixing [11,12] in MQ-MAS experiments on spin $I = 5/2$ nuclei. We note that both the Kentgens' group and the Vega and Frydman groups have recently reported the use of modulated mixing pulses in 3Q-MAS NMR of ^{27}Al [14,15].

The idea behind the X–$\overline{\text{X}}$ pulse train derives from the cosine amplitude modulated mixing period originally proposed by Vega and Naor [16] for 3Q to 1Q conversion in single crystals of spin-3/2 systems and relies on selective irradiation on the satellite transitions. In this Letter, we demonstrate that a similar approach can be applied to higher spin quantum numbers, although, in principle, this requires sequential selective excitation from the outer to inner satellite transitions. Employing this approach, we

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find that significant sensitivity enhancements may be achieved in both 3Q- and 5Q-MAS experiments of ^{27}Al as demonstrated by MQ-MAS spectra for a sample of $NaSi_3AlO_8$. Furthermore, we obtain an approximate doubling of the 3Q-MAS sensitivity for ^{27}Al in $9Al_2O_3 \cdot 2B_2O_3$ compared to conventional (single-pulse mixing) 3Q-MAS experiments.

2. Theoretical background

Using fictitious spin-1/2 operators [16], we represent the 5Q coherences with the operators $I_{\pm}^{1-6}$, the 3Q coherences with $I_{\pm}^{1-4}$, $I_{\pm}^{2-5}$, and $I_{\pm}^{3-6}$, and the central-transition 1Q coherences by $I_{\pm}^{3-4}$. For MQ-MAS we focus on the coherences associated with the symmetric ($m \leftrightarrow -m$) transitions, that is, $I_{\pm}^{1-6}$, $I_{\pm}^{2-5}$, and $I_{\pm}^{3-4}$, as only these are unperturbed by the first-order quadrupolar Hamiltonian.

Our approach is to consider the following rotations in the spin $I = 5/2$ Liouville space,

$$U_{3 \to 1} = \exp\left\{-i\pi\left(I_x^{2-3} + I_x^{4-5}\right)\right\},\qquad(1)$$

$$
\begin{aligned}
U_{5 \to 1} &= U_{3 \to 1}U_{5 \to 3}\\
&= \exp\left\{-i\pi\left(I_x^{2-3} + I_x^{4-5}\right)\right\}\\
&\quad\times \exp\left\{-i\pi\left(I_x^{1-2} + I_x^{5-6}\right)\right\}.
\end{aligned}\qquad(2)
$$

which convert the 3Q ($I_{\pm}^{2-5}$) and 5Q ($I_{\pm}^{1-6}$) coherences into 1Q coherences. That is,

$$U_{3 \to 1}I_{\pm}^{2-5}U_{3 \to 1}^{\dagger} = I_{\pm}^{3-4}\qquad(3)$$

$$U_{5 \to 1}I_{\pm}^{1-6}U_{5 \to 1}^{\dagger} = I_{\pm}^{3-4}.\qquad(4)$$

These equations suggest that an optimum transfer pathway from 3Q → 1Q coherence can be obtained using a selective inversion (π pulse) of the inner ($\pm 3/2 \leftrightarrow \pm 1/2$) satellite transitions. Likewise the optimum 5Q → 1Q coherence transfer pathway is obtained with a selective inversion of the outer ($\pm 5/2 \leftrightarrow \pm 3/2$) satellite transitions followed by a selective inversion of the inner satellites. In practice, these simple schemes for MQ transfer are complicated by differences in the quadrupole splittings for different sites/crystallite orientations. Nonetheless, in the case of spin $I = 3/2$, Madhu et al. [17]

recently showed that an X–$\overline{X}$ pulse train with a fixed modulation frequency can induce such transfers via a rotation-induced *adiabatic* coherence transfer in a similar manner to RIACT [3]. On this basis, we investigated whether an X–$\overline{X}$ pulse train with a fixed modulation frequency near the singularity of the inner satellite transitions could also be used to provide 3Q → 1Q transfers in spin-5/2 systems. Likewise we hypothesized that the sequential application of two X–$\overline{X}$ pulse trains, the first train having a fixed modulation frequency tuned near the singularity of the outer satellite transitions and the second train having a modulation frequency tuned near the singularity of the inner satellite transitions, would provide, in a manner analogous to the propagator in Eq. (2), a more efficient means of generating 5Q → 1Q coherence transfers.

3. Experimental

The experiments presented in this work were performed on Bruker DSX spectrometers with ^{27}Al Larmor frequencies of $\omega_0/2\pi = 78.2$ MHz (DSX-300) and $\omega_0/2\pi = 104.3$ MHz (DSX-400) employing a Bruker 4 mm probehead and with *rf*-field strengths of $\omega_1/2\pi = 90$ kHz for the preparation and mixing pulses while a weaker *rf*-field strength of $\omega_1/2\pi = 20$ kHz was used for the central-transition selective pulses. All spectra were referenced to liquid $Al(H_2O)_6^{3+}$ ($AlCl_3 \cdot 6H_2O$). The natural albite sample, $NaSi_3AlO_8$, has been characterized by XRD to be of Amelia type (JCPDS 20-554). The aluminum borate sample is identical to the one employed in previous MAS and DOR studies [18].

The 3Q-MAS modulated-mixing sequence for a spin-5/2 system is shown in Fig. 1a. This sequence is identical to the shifted-echo sequence that we recently presented to obtain pure absorption-mode lineshapes for spin-3/2 nuclei [20]. In the case of spin-5/2 nuclei, however, it is necessary to employ shifted echo [21,22] acquisition (or symmetrized echo and anti-echo pathways [23,24]) because only the $p = 0 \to +3 \to -1$ coherence pathway is refocussed at positive t_2 values [14,15,20,22]. The modulation frequency, ν_m, is defined as the inverse of the total time to complete one X–$\overline{X}$ interval. In practice, a delay equal in duration to the pulse is inserted
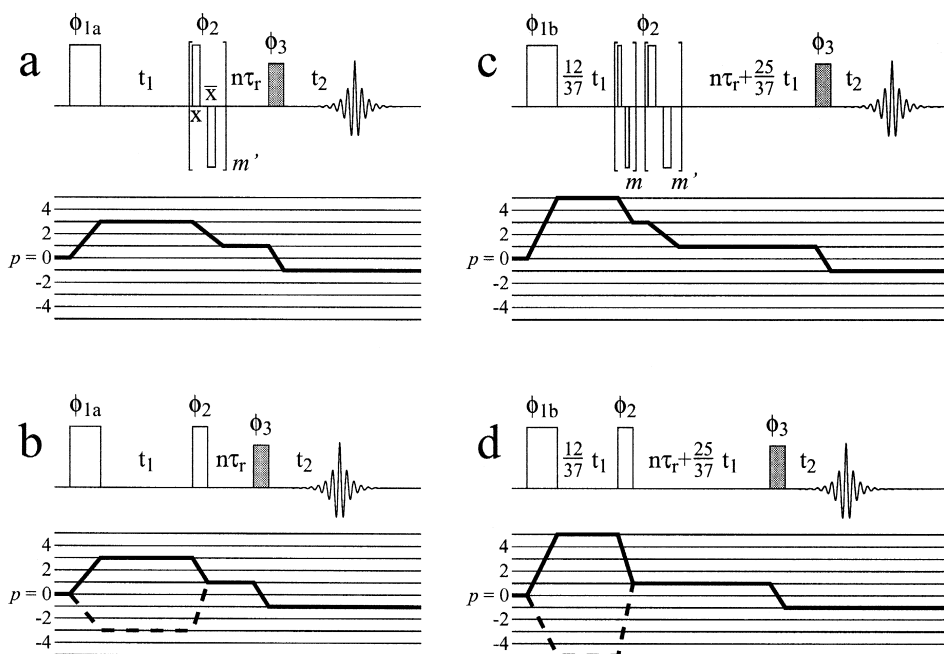
Fig. 1. Timing schemes and coherence transfer pathways for the 3Q-MAS (a,b) and 5Q-MAS (c,d) experiments employing modulated mixing (a,c) or single-pulse mixing (b,d). All sequences employ shifted-echo acquisition (and delayed acquisition [25] for the 5Q-MAS sequences) to ensure pure absorption-mode lineshapes. The three pulses are phase cycled as $\phi_{1a} = 0°, 60°, 120°, \ldots, 300°$ ($\phi_{1b} = 0°, 36°, 72°, \ldots, 324°$) and $\phi_2 = 0°$, supercycled by $\phi_3 = 0°, 180°$, and with the receiver phase adjusted to select the indicated pathways according to standard procedures [19], i.e., $\phi_{rec} = -3\phi_{1a} + 2\phi_3$ or $\phi_{rec} = -5\phi_{1b} + 2\phi_3$.

between each pulse in the X–$\overline{\text{X}}$ pulse train to allow time for the transmitter phase to stabilize. Within the hardware constraints of the spectrometer the modulation frequency is optimized for maximum sensitivity. For the 3Q-MAS modulated-mixing experiment we employed the mixing sequence $[\text{X}(\tau) - \tau - \overline{\text{X}}(\tau) - \tau]_m$ using a modulation frequency of 294 kHz ($\tau = 0.85$ μs), with $m = 4$ for a total mixing period of 13.6 μs, and $\omega_r/2\pi = 10$ kHz (NaSi$_3$AlO$_8$), and a modulation frequency of 357 kHz ($\tau = 0.7$ μs) with $m = 3$ for a total mixing period of 8.4 μs, and $\omega_r/2\pi = 15$ kHz for the sample of 9Al$_2$O$_3$ · 2B$_2$O$_3$. In both cases the total mixing time is approximately one-eighth of a rotor period. For comparison the 3Q-MAS single-pulse mixing sequence with shifted-echo acquisition is shown in Fig. 1b. In this experiment an optimized mixing pulse of length $\tau_{mix} = 1.4$ μs was used for both samples.

The 5Q-MAS X–$\overline{\text{X}}$ modulated-mixing sequence for a spin-5/2 system is shown in Fig. 1c. For the

5Q sequence we use delayed acqustion [25] to obtain pure absorption-mode lineshapes. The 5Q-MAS modulated-mixing sequence is slightly more complicated as the mixing period consists of two X–$\overline{\text{X}}$ pulse trains for the 5Q → 3Q and 3Q → 1Q transfers, respectively. A simple approach to optimize the sensitivity in this experiment is to first optimize the length and modulation frequency of the 3Q → 1Q pulse train by employing the sequence in Fig. 1a and then optimize the frequency and length of the 5Q → 3Q pulse train. The present 5Q-MAS modulated mixing experiment employed the sequence $\{[\text{X}(\tau) - \tau - \overline{\text{X}}(\tau) - \tau]_m - [\text{X}(\tau') - \tau' - \overline{\text{X}}(\tau') - \tau']_{m'}\}$ with modulation frequencies of 625 and 294 kHz ($\tau = 0.4$ μs and $\tau' = 0.85$ μs), respectively, using $m = 6$, $m' = 4$ for totals times of 9.6 μs and 13.6 μs, or approximately one-tenth and one-eighth of a rotor period, respectively. For comparison the 5Q-MAS single-pulse mixing sequence with shifted-echo acquisition is shown in Fig. 1d. In this experiment an

optimized mixing pulse of length $\tau_{mix} = 1.5$ μs was used.

4. Results and discussion

To demonstrate the improved sensitivity performance of the MQ-MAS sequences with X–$\overline{\text{X}}$ mixing we used the four sequences in Fig. 1 for ^{27}Al on a sample of natural $NaSi_3AlO_8$ ($\omega_r/2\pi = 10$ kHz), which exhibits one site with $C_Q = 3.2$ MHz. Fig. 2 (a–d) shows the cross-sections through the isotropic resonance of the single site for the four different pulse sequences in Fig. 1 and the complete 2D spectrum (Fig. 2e) recorded employing the 3Q-MAS modulated mixing sequence in Fig. 1a. The four cross-sections in Fig. 2a–d are acquired employing the pulse sequences in Fig. 1a–d, respectively. Indeed we observe significant gains in sensitivity by employing modulated mixing (a,c) over the single-pulse mixing spectra (b,d) under the current experimental conditions. The most significant gain is observed for the double-modulated 5Q → 1Q mixing over the single-pulse mixing sequence. We note that the sensitivity of the 5Q-MAS experiments is lower than in the 3Q-MAS experiments. Moreover, the 5Q-MAS experiments reveal a significant distortion of the second-order quadrupolar lineshape, caused by the inhomogeneous 5Q coherence excitation (and 5Q → 1Q mixing) for the different crystallite orientations. Therefore, the applicability of the 5Q-MAS experiment will still be limited by a low sensitivity [26]. However, it will often be of interest to perform 5Q-MAS rather than 3Q-MAS experiments since 5Q-MAS provides a larger dispersion of isotropic chemical shifts in the isotropic dimension than 3Q-MAS. In this context we note that a very recent study has demonstrated that the optimum dispersion of chemical shifts is achieved by combining evolutions under 5Q and 3Q coherences in the indirect dimension [27].

4.1. ^{27}Al MQ-MAS NMR of $9Al_2O_3 \cdot 2B_2O_3$

$9Al_2O_3 \cdot 2B_2O_3$ is a binary oxide that has previously been intensively studied by ^{27}Al solid-state NMR [18,28–30]. This compound is of particular
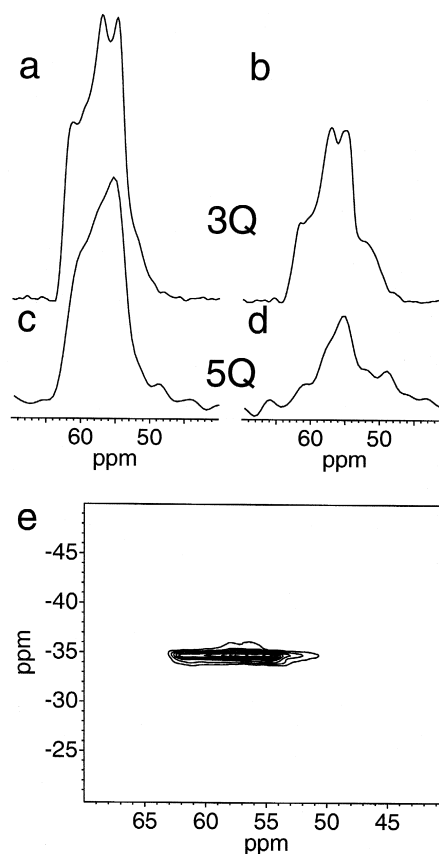

Fig. 2. ^{27}Al MQ-MAS experiments of $NaSi_3AlO_8$ illustrating the sensitivity improvement obtained by the modulated-mixing sequences in Fig. 1. The cross-sections in a, b, c, and d are acquired employing the 3Q modulated mixing (Fig. 1a) sequence, the 3Q single-pulse mixing (Fig. 1b) sequence, the 5Q modulated mixing (Fig. 1c) sequence, and the 5Q single-pulse mixing (Fig. 1d) sequence, respectively. Note that the 3Q-MAS and 5Q-MAS spectra are not plotted with the same vertical scale. The contour plot (e) represents the full two-dimensional spectrum of the 3Q modulated mixing experiment. The contours are drawn at 10, 20, …, and 90% of the maximum intensity.

interest for high-resolution ^{27}Al NMR because of the presence of four Al sites with different coordination numbers (Al_{IV} : one site, Al_V : two sites, and Al_{VI} : one site with double intensity) [31]. Although the quadrupole coupling parameters and isotropic chemical shifts have already been reported for all four aluminum sites, we still found this material a challenge for an ^{27}Al MQ-MAS NMR study because of the relatively strong quadrupolar couplings (C_Qs in
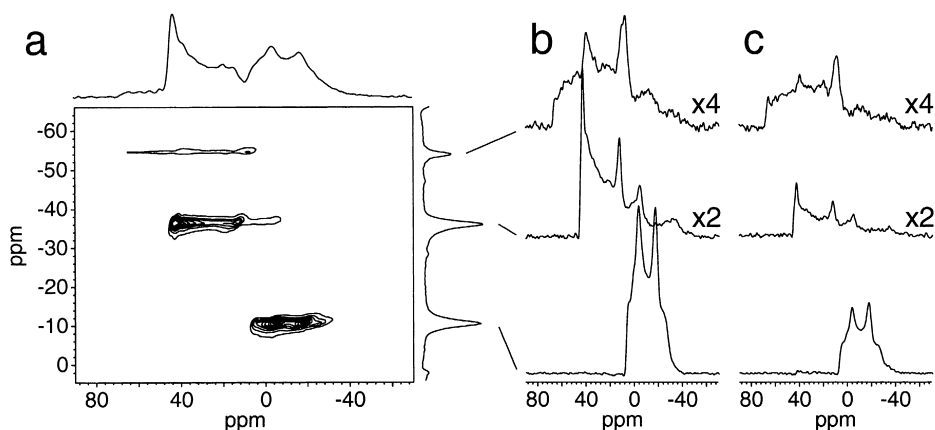
Fig. 3. (a) Two-dimensional ^{27}Al 3Q-MAS spectrum of $9Al_2O_3 \cdot 2B_2O_3$ recorded at 9.4 T employing the modulated-mixing sequence in Fig. 1a. The isotropic projection reveals three distinct resonances. The cross-sections through these resonances (b) show well-defined second-order quadrupolar lineshapes for the sites located at approximately -56 and -12 ppm in the isotropic dimension while the cross-section of the resonance at -37 ppm displays two partly overlapping sites. The cross-sections in (c) result from the spectrum recorded using the single-pulse mixing sequence in Fig. 1b and plotted on the same vertical scale as the corresponding modulated-mixing cross-sections in (b).

the range of 6–9 MHz) which will cause very low intensities in regular MQ-MAS experiments.

Figs. 3 and 4 display the ^{27}Al 3Q-MAS spectra of $9Al_2O_3 \cdot 2B_2O_3$ recorded at 9.4 and 7.1 T, respectively, with a sample spinning rate of $\omega_r/2\pi = 15$

kHz. In both spectra we note a clear separation of the Al_{IV}, Al_V, and Al_{VI} sites. The isotropic projection of the 7.1 T spectrum (Fig. 4) reveals the presence of four sites in accordance with the crystal symmetry [31] and previous NMR studies [18,29]. For the
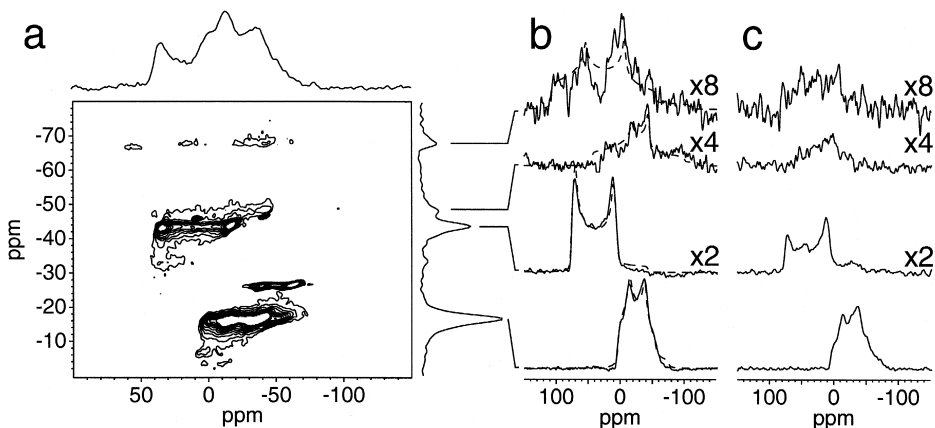

Fig. 4. (a) Two-dimensional ^{27}Al 3Q-MAS spectrum of $9Al_2O_3 \cdot 2B_2O_3$ recorded at 7.1 T employing the modulated-mixing sequence in Fig. 1a. The isotropic projection reveals four distinct resonances at approximately -68, -48, -44, and -16 ppm. The cross-sections through all four resonances (b) show well-defined second-order quadrupolar lineshapes. The cross-sections in (c) result from the spectrum recorded using the single-pulse mixing sequence in Fig. 1b and plotted on the same vertical scale as the corresponding modulated-mixing cross-sections in (b). For illustration of the quality of the spectrum the best-fit simulations are shown by dashed lines in (b).

Table 1

^{27}Al quadrupole couplings (C_Q, η_Q) and isotropic chemical shifts (δ_{iso}) for the four aluminum sites in $9Al_2O_3 \cdot 2B_2O_3$ determined from the present ^{27}Al MQ-MAS study and previous MAS and DOR studies

Site	C_Q (MHz)	η_Q	δ_{iso} (ppm)	Reference
Al$_{IV}$	9.1 ± 0.1	0.44 ± 0.02	71 ± 1	This work [a]
	8.9	0.42	70	[29] [b]
	9.0	0.45	71	[18]
Al$_V$ (1)	8.0 ± 0.1	0.70 ± 0.05	44 ± 1	This work [a]
	7.1	0.49	43	[29] [b]
	7.9	0.7	44	[18]
Al$_V$ (2)	6.8 ± 0.1	0.08 ± 0.02	52 ± 1	This work [a]
	9.4	0.02	52	[29] [b]
	6.8	0.06	52	[18]
Al$_{VI}$	5.75 ± 0.05	0.39 ± 0.02	8 ± 1	This work [a]
	6.0	0.45	8	[29] [b]
	6.0	0.40	8.6	[18]

[a] The parameters represent weighted averages for the two magnetic field strengths (7.1 and 9.4 T) employed in this study.

[b] The parameters listed are averages of the parameters determined from the 156 and 104 MHz spectra in Ref. [29].

spectrum recorded at 9.4 T (Fig. 3), however, the two Al$_V$ sites both resonate at approximately -37 ppm and are still partly overlapping in the cross-section through this resonance (Fig. 3b). The cross-sections through the isotropic resonances reveal that the intensity of the spectra recorded with modulated mixing (Fig. 3b and Fig. 4b) is approximately doubled relative to the single-pulse mixing spectra in Fig. 3c and Fig. 4c.

The higher sensitivity of the modulated-mixing spectra in Figs. 3 and 4 allows us to determine the quadrupole coupling parameters and isotropic chemical shifts for all four sites with quite good precision. These parameters are summarized in Table 1 which, for comparison, also includes the parameters determined from previous MAS and DOR studies [29,18]. We find that all parameters for all four sites are in very good agreement with those of the previous studies [29,18] except slight disagreements with the parameters from Ref. [29] on the parameters for site Al$_V$ (1).

5. Conclusion

We have demonstrated that an X–$\overline{\text{X}}$ pulse train can also be employed during the mixing period of the MQ-MAS experiment on spin-5/2 nuclei to enhance the spectral sensitivity. For the case of 5Q-MAS, the sequential application of two X–$\overline{\text{X}}$ pulse trains with different modulation frequencies are employed for the 5Q → 1Q mixing. Using this approach we have obtained an approximate doubling of the sensitivity for ^{27}Al 3Q-MAS and 5Q-MAS spectra of polycrystalline NaSi$_3$AlO$_8$ and $9Al_2O_3 \cdot 2B_2O_3$.

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