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# Enhanced $^{29}Si$ spin-lattice relaxation and observation of three-dimensional lattice connectivity in zeolites by two-dimensional $^{29}Si$ MASS NMR

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**Abstract.** It is shown that considerable sensitivity enhancement is achieved in the $^{29}Si$ MASS NMR spectra of highly siliceous zeolites by pretreating the material with oxygen. The presence of adsorbed molecular oxygen in zeolite channels promotes an efficient $^{29}Si$ spin-lattice relaxation via a paramagnetic interaction between the lattice $^{29}Si$ *T*-site and the adsorbed oxygen on zeolite channels. This affords an efficient 2-D data collection and leads to increased sensitivity. The utility of this method is demonstrated in a two-dimensional COSY-45 NMR experiment of a high silica zeolite ZSM-5.

**Keywords.** $^{29}Si$ MAS NMR; $^{29}Si$ $T_1$; zeolites; ZSM-5; *T*-sites.

## 1. Introduction

Highly siliceous zeolites contain $Si(O_4)_{0\cdot5}$ tetrahedra interlinked through oxygen bridges to form a high surface area structure and contain intracrystalline cavities and channels of molecular dimensions (Breck 1974). Silicalite and the closely related ZSM-5 zeolites (Budiansky 1982) serve as industrially important catalysts as they provide a potential route for synthetic fuels (Chang 1983). Among the various experimental techniques used to probe the zeolite framework structure, solid state NMR spectroscopy has emerged as a powerful method (Engelhardt and Michel 1987).

In high-silica materials exhibiting a very high degree of crystallinity, the $^{29}Si$ Magic Angle Sample Spinning (MASS) spectrum can be recorded with an increased spectral resolution (Fyfe *et al* 1982, 1984), thus aiding in the inspection of the crystallographic multiplicity of the lattice silicon in tetrahedral coordination. We have recently shown that important synthetic and crystal growing considerations apply to high silica zeolites and that a very high degree of crystallinity, devoid of the amorphous defect phase, is a prerequisite before an NMR inspection is made (Sivadinarayana *et al* 1994). Also, only in such materials is a routine application of two-dimensional (2-D) $^{29}Si$ MASS NMR experiments for establishing three-dimensional lattice connectivities feasible.

Fyfe *et al* (1990, 1991) have recently applied 2-D NMR techniques (Chandrakumar and Subramanian 1987), such as COSY, INADEQUATE etc., to establish 3-D lattice

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connectivity in high-silica zeolites, such as ZSM-11, ZSM-39, ZSM-5 etc. Despite the low natural abundance of $^{29}Si$ (4·8%), the 2-D correlation could be established in unenriched materials through the isotropic $J_{Si-Si}$ scalar interactions ($\approx 15$ Hz) between adjacent lattice silicons by means of a coherence transfer mechanism (Müller *et al* 1975). However, a major limitation in these studies has been the enormously long time (as long as 116 h, Fyfe *et al* 1990) spent in the 2-D data collection. This is mainly due to a prohibitively long spin-lattice relaxation time for $^{29}Si$ in the highly crystalline phase, necessitating employment of long recycle times ($\geq 30$ s). This undoubtedly restricts a routine application of $^{29}Si$ 2-D MASS NMR to highly siliceous materials, since stable experimental conditions are hard to maintain over such long periods of signal accumulation. It is therefore worthwhile if this is circumvented to increase the inherent sensitivity of repetitive 2-D experiments.

In highly siliceous materials devoid of defect sites (Si(OH), $Si(OH)_2$), it is understood that an efficient mechanism for the $^{29}Si$ spin-lattice relaxation does not exist. This stems from the fact that spin–spin interactions (Si–Si) are very weak and, additionally, there are no lattice motions which can effectively modulate them at the Larmor frequency. In uncalcined samples containing organic templates, the $^{29}Si$ $T_1$ problem

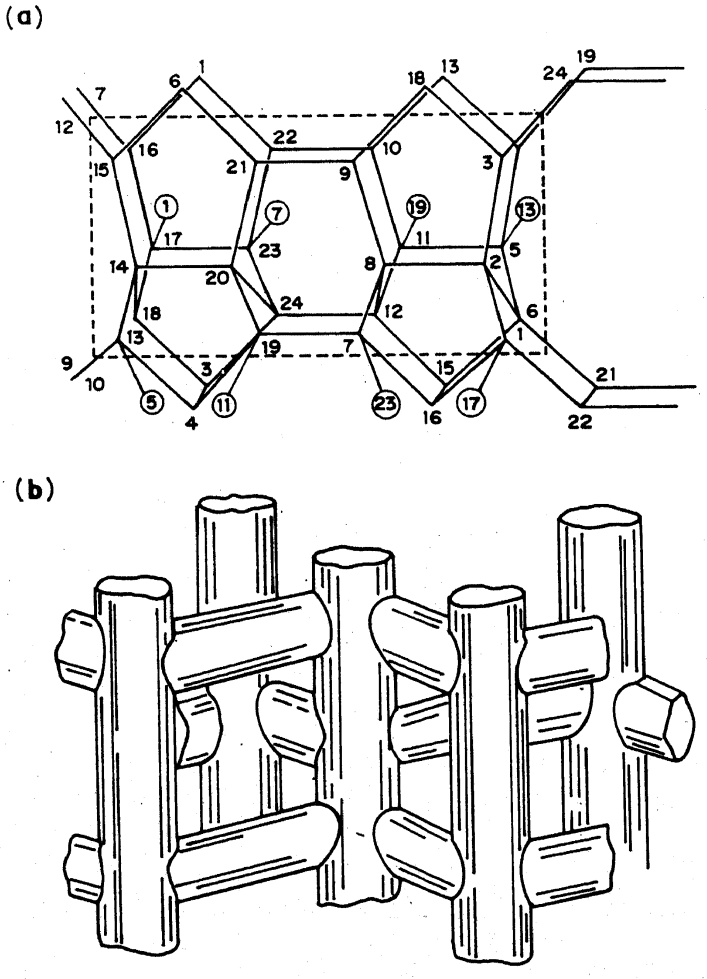


**Figure 1.** (**a**) Asymmetric unit in the monoclinic phase of ZSM-5 showing the twenty-four crystallographically nonequivalent *T*-sites. (**b**) Channel structure of ZSM-5 showing straight and sinusoidal channels.

is alleviated to a great extent by taking recourse to $^{1}H$–$^{29}Si$ CP-MASS method. This, besides restricting application to only template-containing silicalites, however, requires double resonance hardware and precise setting of Hartmann–Hahn match conditions (Hartmann and Hahn 1962). We show herein that for the Bloch decay observation of $^{29}Si$, a recourse can be sought by adsorbing molecular oxygen on the zeolite channels which acts as a relaxation sink for $^{29}Si$. This, in turn, leads to an increased sensitivity in the 2-D MASS NMR experiments for establishing structural correlation among various lattice *T*-sites. Figure 1 shows a representative schematic of the molecular (a) and channel (b) structure of zeolite ZSM-5 into which molecular oxygen could be adsorbed.

## 2. Experimental

### 2.1 *Preparation and treatment of high silica ZSM-5*

High silica ZSM-5 with Si/Al $>$ 10,000 (silicalite-I) was prepared by hydrothermal synthesis from a gel of composition, template:$SiO_2$:$H_2O$ = 1:70:107 at 443 K for a period of 8 days (Sivadinarayana *et al* 1994). During crystallization the autoclave was stirred occasionally. The zeolite crystals were washed thoroughly, dried at 373 K, and calcined in static air at 813 K for 6 h. They were then treated with 0·1 M HCl at 353 K thrice to remove traces of amorphous mass, dried and calcined at 813 K for 6 h. The synthesized material was subsequently characterized by XRD (Philips PW 1730), FT-IR (Perkin Elmer 1600) and SEM (JEOL-5420) and was found to conform to the monoclinic phase of high silica ZSM-5 (van Koningsveld *et al* 1990). The silicalite was evacuated for 6 h before atmospheric pressure was established using dry oxygen from a gas cylinder and passing it over the sample in a quartz reactor at 673 K for 12 h. The zeolite was subsequently transferred to a 7 mm zirconia MASS rotor under oxygen blanket. The top layer of zeolite in the rotor was covered with a teflon tape before an air-tight KEL-F cap was fitted on to the rotor.

### 2.2 *$^{29}Si$ MASS NMR*

MASS NMR experiments were performed at 59·826 MHz on a Bruker MSL-300 FT-NMR spectrometer at ambient probe temperature (295 K), $^{29}Si$ $T_1$ measurements were carried out using a saturation recovery pulse sequence. The $\pi/2$ pulse was 4 $\mu$s. MASS was usually kept at around 3 kHz. For the 2-D experiments, a COSY-45 pulse sequence was employed in order to reduce the diagonal intensity and to improve the clarity of cross-peaks lying close to the diagonal. A recycle time of 600 ms was used while collecting the 2-D data set. The total measurement time for the 2-D experiment was approximately 6·2 h.

## 3. Results and discussion

The recovery of the $^{29}Si$ signal in the $T_1$ experiment of one of the *T*-sites in the high silica ZSM-5 is shown in figure 2a. The magnetisation recovery is seen to be a two-step process, namely, an initial rapid recovery followed by a much slower build-up of the

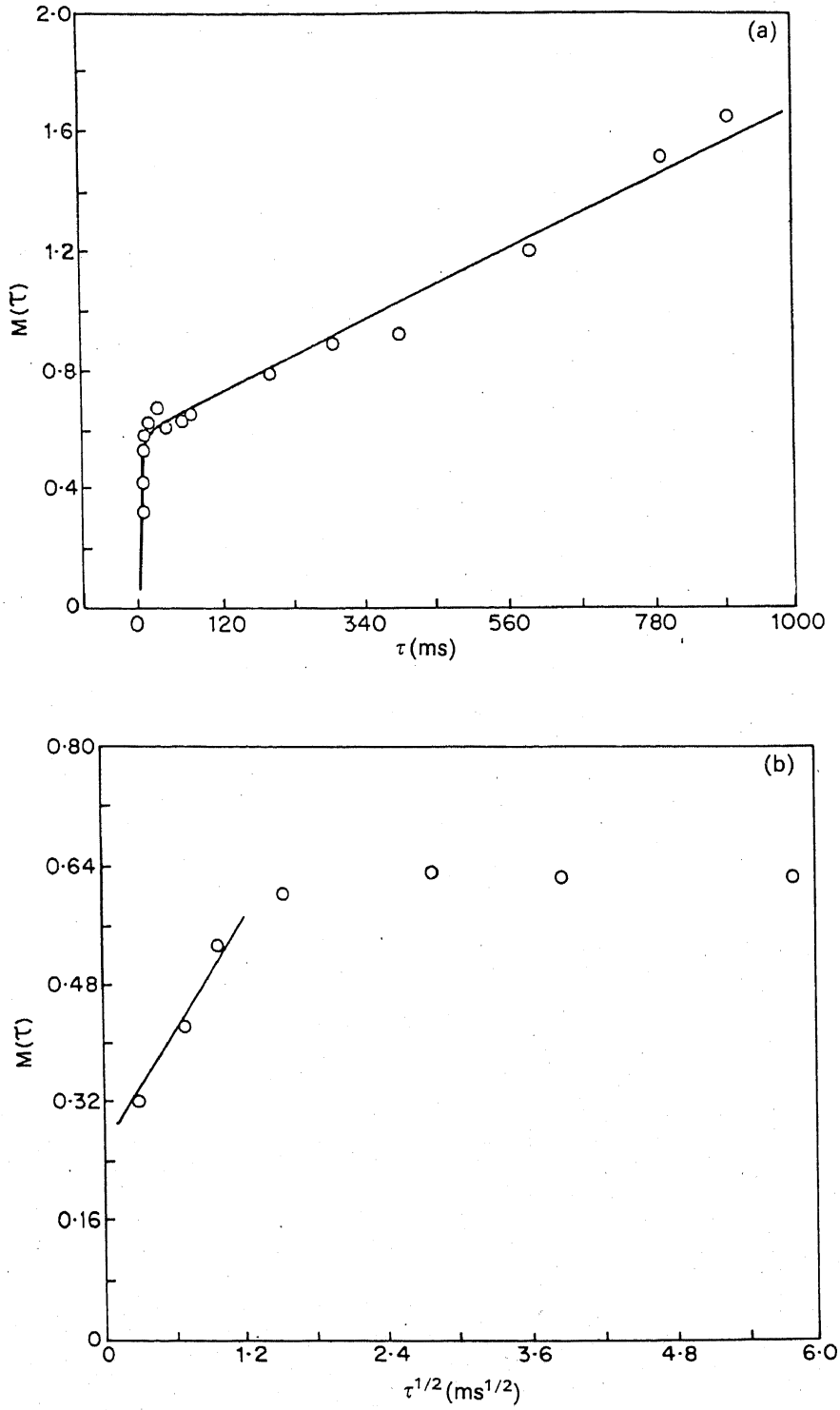


**Figure 2.** (**a**) Overall recovery of the longitudinal $^{29}Si$ magnetisation for a tetrahedral site following complete saturation. $\tau$ denotes the delay between the saturation comb and the monitoring $\pi/2$ pulse. The solid line has been drawn to show the initial rapid recovery followed by a slow growth to equilibrium. (**b**) The initial part of the magnetisation recovery showing $t^{1/2}$ dependence.

longitudinal magnetisation to its equilibrium value. Further, the initial part of the recovery has a $t^{1/2}$ dependence (figure 2b), whereas at long times it is exponential.

The spin-lattice relaxation of $^{29}Si$ may be thought to occur via a paramagnetic dipolar interaction between silicon and the molecular oxygen present in the channels. Klinowski (1986) has examined the various contributions to $T_1$ and reported that the presence of oxygen in air is indeed the principal factor. It has been shown that displacement of air in the zeolite channels by nitrogen or by organic species increases $^{29}Si$ relaxation times (Cookson and Smith 1985). Therefore, deliberate adsorption of oxygen on zeolite channels can significantly enhance the spin-lattice relaxation process. This arises from the net paramagnetism associated with the unpaired electron spins of $\Pi^*$ ($2p$) molecular orbitals of oxygen, which gives rise to a through-space dipolar interaction with the lattice silicon. This interaction is expected to be the strongest for $T$-sites adjacent to the cage walls, where the effect is to depress $^{29}Si$ $T_1$ greatly. The transport of the spin energy to remote silicons (interior $T$-sites) occurs via a limited spin-diffusion process when the low natural abundance of silicon and the partial quenching due to MASS are considered (Blumberg 1960; Fukushima and Vehling 1968; Lowe and Tse 1968; Iwamiya and Gerstein 1986). Under these conditions, the approximate short time behaviour is governed by

$$M(\tau) = 4\pi^{3/2} NC^{1/2} \tau^{1/2}, \tag{1}$$

where $N$ is the number of paramagnetic centres per $cm^3$ and $C$ represents the strength of the electron–nuclear interactions. The long time behaviour has the form

$$M(\tau) = M_0[1 - \exp(-\tau/T_1)]. \tag{2}$$

At short $\tau$, $M(\tau)$ starts out with a $t^{1/2}$ dependence and proceeds to an exponential dependence. While the apparent $T_1$ in (2) appears to be long for the magnetization recovery, a sizeable portion of $^{29}Si$ spins have already recovered as indicated by (1).

The predicted initial $t^{1/2}$ dependence is clearly borne out from the experimental data of figure 2b. The long-term exponential behaviour is also noticed in figure 2a and these data points project the spin-lattice relaxation time in the several tens of seconds range. The rapidly recovered magnetization along the $z$-axis at early times can be used to build up a time-averaged signal over much shorter accumulation times. The general utility of this approach is demonstrated in figure 3, where a contour plot of the 2-D data acquired on the high-silica ZSM-5 is shown. We also show above this plot the resolution enhanced $^{29}Si$ MASS spectrum of the high-silica ZSM-5. Considering the overlap of some peaks which are not resolved, the entire spectral manifold can be resolved into twenty-four crystallographically inequivalent $T$-sites in the monoclinic crystalline phase (van Koningsveld *et al* 1990). The crystallographic multiplicity has been ascribed to the variation in $T$-site geometry through its effects on the $^{29}Si$ chemical shift (Skibsted *et al* 1990).

From the 2-D contour plot (figure 3) we can establish the various lattice connectivities of the crystallographically non-equivalent $T$-sites. The various X-ray determined (van Koningsveld *et al* 1990) $T$-site connectivities are given in table 1. The most conspicuous and directly readable ones are marked in figure 3. These represent $T$-site connectivities between well-resolved and unambiguously-assigned $^{29}Si$ resonances within the repeat unit of the zeolite. However, many of the resonances occurring in the restricted range of 113–113·8 ppm give rise to cross-peaks which lie very close to

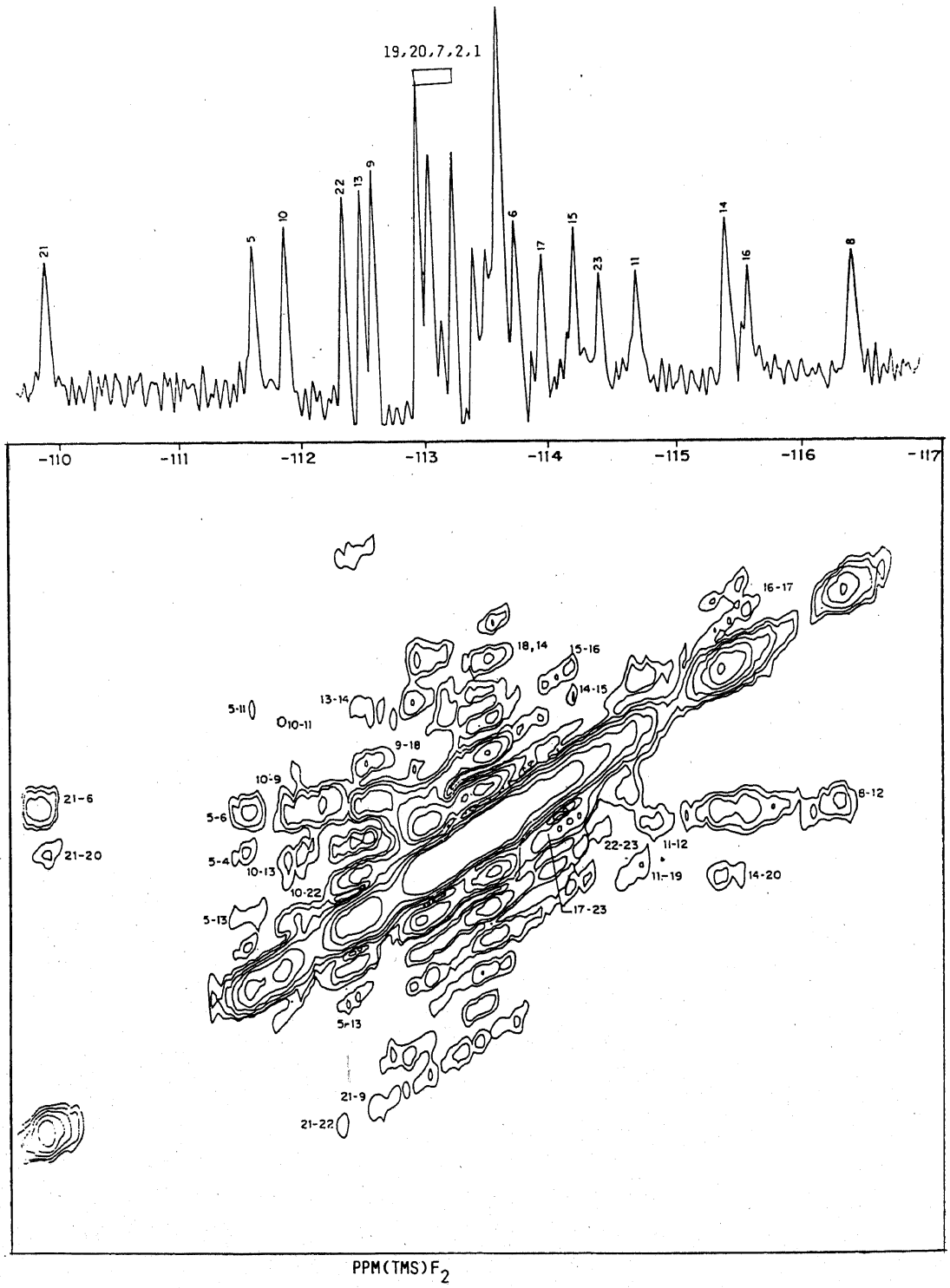


**Figure 3.** Contour plot of the rapidly pulsed 2-D COSY-45 experiment. A resolution enhanced 1-D MASS spectrum is shown on top. The *T*-site connectivities that could be readily identified are indicated. The 2-D data set comprises 56 experiments with a $t_1$ increment of 403 $\mu$s in a 1240 Hz spectral window. Number of scans = 640. Total 2-D measurement time = 6 h. The 2-D data was processed using a Gaussian window function in both dimensions.

**Table 1.** X-ray determined *T*-site connectivities in silicalite-I[+].

| *T*-site | Connectivity | *T*-site | Connectivity |
|---|---|---|---|
| 1 | 1–2, 1–6, 1–17, 1–22* | 13 | 13–4*, 13–5*, 13–10*, 13–14* |
| 2 | 2–1, 2–3, 2–6, 2–8 | 14 | 14–13*, 14–15*, 14–18*, 14–20 |
| 3 | 3–2, 3–4, 3–18, 3–24 | 15 | 15–6*, 15–12, 15–14*, 14–16* |
| 4 | 4–3,4–5*, 4–13, 4–19 | 16 | 16–1, 16–7, 16–15*, 16–17* |
| 5 | 5–4*, 5–6*, 5–11*, 5–13* | 17 | 17–1, 17–16*, 17–18, 17–23* |
| 6 | 6–2, 6–5*, 6–15*, 6–21* | 18 | 18–3, 18–9*, 18–14*, 18–17 |
| 7 | 7–8, 7–16, 7–19, 7–23 | 19 | 19–4, 19–7, 19–11*, 19–20 |
| 8 | 8–2, 8–7, 8–9, 8–12* | 20 | 20–14, 20–19, 20–21*, 20–24 |
| 9 | 9–8, 9–10*, 9–18*, 9–21* | 21 | 21–6*, 21–9*, 21–20*, 21–22* |
| 10 | 10–9*, 10–11*, 10–13*, 10–22* | 22 | 22–1*, 22–10*, 22–21*, 21–23* |
| 11 | 11–5*, 11–10*, 11–12*, 11–19* | 23 | 23–7, 23–17*, 23–22*, 23–24 |
| 12 | 12–8*, 12–11*, 12–15, 12–24 | 24 | 24–3, 24–12, 24–20, 24–23 |

Connectivities shown by an asterisk are clearly identified and marked in figure 2.
[+] Reference: Fyfe *et al* (1990).

the diagonal and are therefore not directly readable from figure 3. Moreover, the 2-D contour resolution suffers from the magnitude mode of data processing that we have employed. The overall cross-peak resolution can be greatly improved by employing phase-sensitive double quantum-filtering strategies. Even greater sensitivity enhancement may be achieved by performing rapidly pulsed experiments using large MASS rotors at higher magnetic field strengths.

We have shown that the short-term behaviour of the longitudinal $^{29}Si$ magnetisation obeys $t^{1/2}$ behaviour when molecular oxygen is adsorbed on the zeolite channels. The signal build-up due to repetitive averaging of the rapid initial recovery of $^{29}Si$ magnetisation affords efficient data collection. An example is presented in the COSY-45 experiment conducted on a highly siliceous zeolite ZSM-5. Since zeolites have a pore structure, enhancement of spin-lattice relaxation by adsorbing molecular oxygen on the channels is a useful strategy to increase sensitivity in 2-D experiments.

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