

Communication

An application of the XiX decoupling for solid state ^{13}C NMR with mobile samples

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Abstract

It is very important to obtain higher resolution solid state NMR spectra not only for crystal samples but also for mobile solid samples. We demonstrate that a robust proton decoupling technique, XiX (X inverse-X) decoupling, is very effective in high resolution solid state NMR measurement for mobile samples compared with the usual continuous wave proton decoupling.

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1. Introduction

It is very important to obtain high resolution spectra in order to analyze detailed local structures and dynamics of molecules by NMR spectroscopy not only for liquids, but also for solids [1–3]. Especially, in ^{13}C NMR for organic molecules, the heteronuclear spin–spin coupling among the observed ^{13}C nucleus and protons should be removed for high resolution NMR.

In solution NMR, proton decoupling schemes are well developed [4] and the resolution is normally limited by the relaxation of the samples. On the other hand, in high resolution solid state ^{13}C NMR, magic angle spinning (MAS) and high power proton decoupling techniques are normally used to reduce anisotropic interactions, such as chemical shift and heteronuclear dipolar interaction, which are averaged out by fast isotropic motion in the liquid state. For proton decoupling, continuous wave (CW) has been used for the purpose. However, recently, several new decoupling schemes using phase, amplitude, and/or frequency modulations have been developed, such as two-pulse phase modulated (TPPM) [5], FMPM [6], and AM-TPPM [7] decoupling schemes. Most recently, XiX (X inverse-X) decoupling was presented by Detken

et al. [8]. XiX decoupling scheme consists of continuous irradiation with pulses of pulse width, t_p , and phase difference of 180° as shown in Fig. 1. This XiX decoupling has an advantage over the other techniques [9]; there is only single parameter, t_p , to be adjusted, however other techniques need at least two parameters to be adjusted. The original idea of the XiX decoupling was reported previously [10,11], however Detken et al. demonstrated the advantage of the XiX decoupling for crystalline samples at high spinning speed (above ca. 20 kHz) and at high proton decoupling power (above ca. 100 kHz). However, it is not easy to accomplish such a severe NMR experimental condition.

In this work, we demonstrate that XiX decoupling is very effective for mobile samples at lower spinning speed (less than 15 kHz) and at lower proton decoupling power. For mobile samples, a long acquisition period with proton decoupling is required and therefore lower power proton decoupling is really necessary in order to avoid great damage to the NMR spectrometer by high power proton decoupling.

2. Methods

All ^{13}C solid state NMR experiments were performed with Varian UNITYINOVA 400 MHz spectrometer

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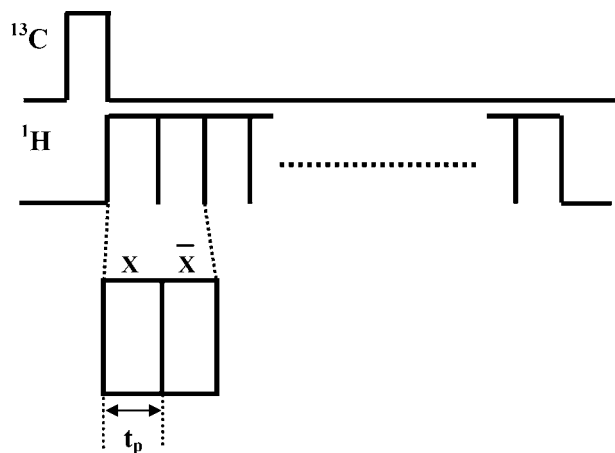


Fig. 1. ^{13}C MAS NMR pulse sequence and XiX decoupling scheme. The XiX decoupling consists of the continuous irradiation of pulse width t_p and opposite phase.

with 5 mm AutoMAS DR and 4 mm T3 DR probes. The sample spinning speeds were stabilized in ± 5 Hz.

3. Results

As mentioned above, t_p in XiX decoupling should be adjusted to obtain higher resolution as much as possible. Adamantane ^{13}C MAS spectrum with normal CW decoupling at 5 kHz sample spinning speed and 50 kHz proton decoupling power is shown in Fig. 2a. Fig. 2b shows the dependence of the heights of methylene peak of adamantane on the pulse width of XiX decoupling at 5 kHz sample spinning speed and 50 kHz proton decoupling power. The peak heights are normalized to those of CW decoupling at the same sample spinning speed and proton decoupling power. As reported by Detken et al. [8], strong decoupling occurred and the intensities of the peaks reduced at $t_p = n \times 1/4t_r$, when sample spinning speed is very fast (30 kHz). Here n is an integer and t_r is a rotor period. For a broad range of t_p/t_r , the peak height with XiX decoupling is higher than that with CW decoupling, which is indicated by a horizontal dashed line in Fig. 2b in the region of $t_p/t_r > 0.5$. Therefore, when t_p is carefully adjusted, XiX decoupling gives higher peak intensity—which normally means higher resolution—compared with CW decoupling. For example, when $t_p = 2.85 \times t_r$ was used for XiX decoupling, the linewidth (full width of half height: FWHH) of methylene peak is 3.8 Hz, but 4.7 Hz for CW decoupling at 50 kHz proton decoupling. Furthermore, the gain in peak heights of both methylene and methine peaks with XiX decoupling is 10% higher than CW decoupling.

Fig. 3 shows the dependence of (a) the peak heights and (b) FWHH of the methylene carbon of adamantane on the proton decoupling power. A dashed line shows

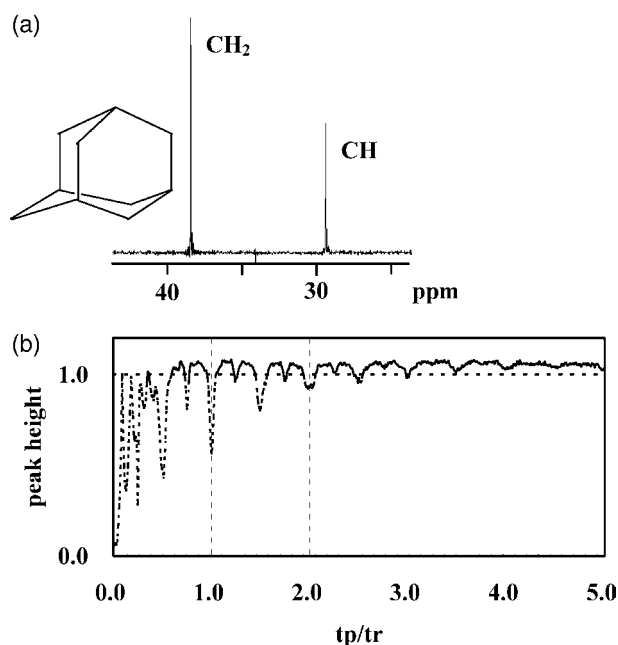


Fig. 2. (a) Adamantane ^{13}C MAS spectra with CW decoupling at 5 kHz sample spinning speed and 50 kHz proton decoupling power. (b) The dependence of the heights of methylene peak of adamantane on the pulse width (t_p) of XiX decoupling at 5 kHz sample spinning speed and 50 kHz proton decoupling power, where t_r is a rotor period. Each peak height is normalized to that with CW decoupling at the same sample spinning speed and proton decoupling power.

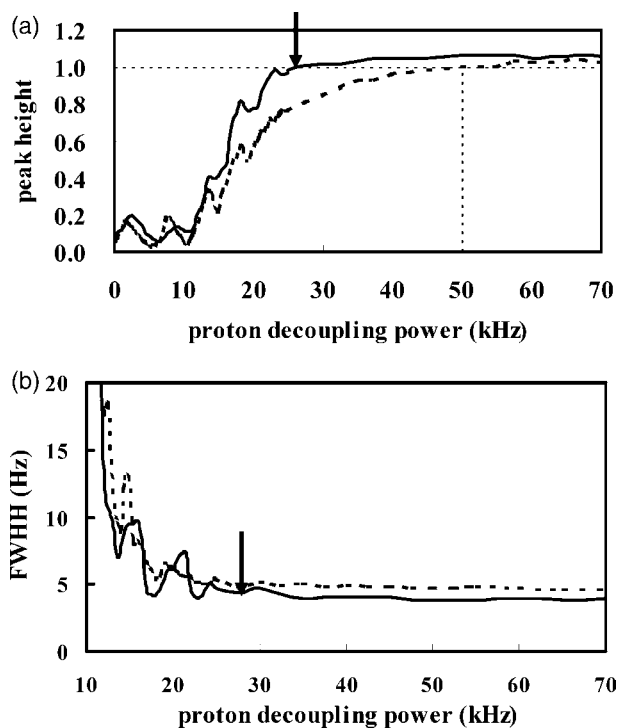


Fig. 3. The dependence of (a) the peak heights and (b) FWHH of methylene carbon of adamantane on XiX (rigid) and CW (dash) proton decoupling powers. Each peak height is normalized to that of 50 kHz CW decoupling power (the horizontal dashed line in (a)).

CW and rigid line shows XiX decoupling. The rotary resonance effect is obvious at $\omega_{rf} = \omega_r \times n$ for both decoupling schemes in Fig. 3a [12], where ω_{rf} is proton decoupling power and ω_r is sample spinning speed. It is obvious that XiX decoupling gives much higher peak height and narrower linewidth compared with CW decoupling at almost all proton decoupling power except rotary resonance conditions. Furthermore, the obtained peak height and FWHH (4.7 Hz) of methylene carbon with 28 kHz XiX decoupling (indicated as an arrow in Figs. 3a and b) are the same as those with 50 kHz CW decoupling. Therefore with XiX decoupling, the same resolution can be obtained at lower power compared with CW decoupling.

Detken et al. applied XiX decoupling to crystalline glycine and alanine at >30 kHz sample spinning speed. However, for adamantane, we demonstrated that XiX decoupling was also effective at much slower sample spinning speed. Considering these results, the efficiency of the XiX decoupling seems to depend on the mobility of the samples.

To verify this concept, we applied XiX decoupling to another very mobile sample, natural rubber (*cis*-polyisoprene), at 6 and 15 kHz sample spinning speeds. At 6 kHz sample spinning, the *J*-resolved high resolution spectrum could be obtained at ^{13}C MAS experiment without proton decoupling. Therefore, 6 kHz sample spinning is enough to decrease ^{13}C - ^1H dipolar coupling effectively and the internal mobility of natural rubber is very fast. Fig. 4 shows the ^{13}C MAS spectra of natural rubber at 6 kHz sample spinning speed with (a) CW and (b) XiX decoupling at 80 kHz proton decoupling power. For XiX decoupling, t_p was carefully adjusted as $2.6 \times t_r$. The peak intensities are higher at XiX decoupling compared with CW decoupling. Especially, the intensity of the methyl peak increased about 8% which was a remarkable point.

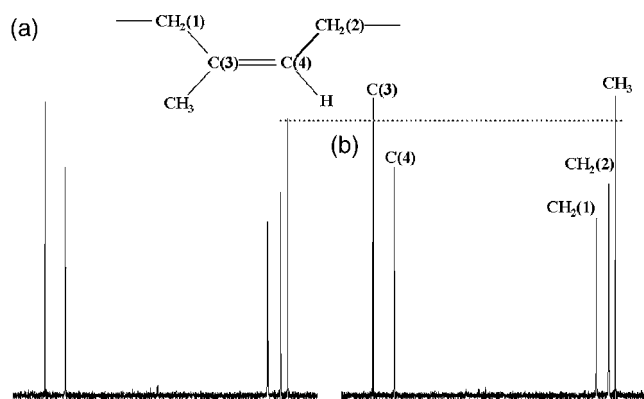


Fig. 4. Natural rubber (*cis*-polyisoprene) ^{13}C MAS spectra with (a) CW and (b) XiX decoupling at 6 kHz sample spinning speed and 80 kHz proton decoupling power. The dashed horizontal line shows the methyl peak height with the CW decoupling.

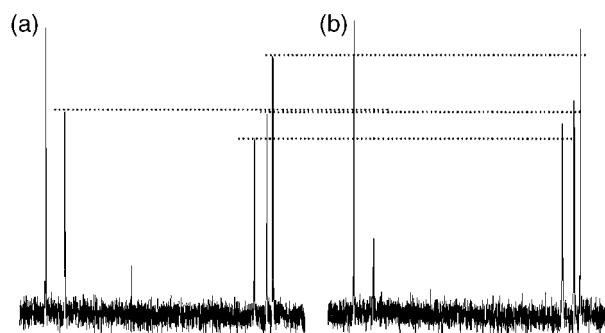


Fig. 5. Natural rubber (*cis*-polyisoprene) ^{13}C MAS spectra with (a) CW and (b) XiX decoupling at 15 kHz sample spinning speed and 80 kHz proton decoupling power. The dashed horizontal line shows the peak height with the CW decoupling.

Table 1

The full width of half height (FWHH) of each carbon peak in ^{13}C MAS spectra of natural rubber with XiX decoupling at 6 kHz (Fig. 4b) and 15 kHz (Fig. 5b) sample spinning speeds under 80 kHz proton decoupling power

Spinning speed (kHz)	C(3)	C(4)	CH ₂ (2)	CH ₂ (1)	CH ₃
6	98.8	100.2	97.8	98.9	95.7
15	92.4	85.2	101.0	99.1	86.1

The FWHH values are listed relative to those with CW decoupling (normalized as 100.0) observed at the same sample spinning speed.

Fig. 5 shows that the ^{13}C MAS spectra of natural rubber at 15 kHz sample spinning speed with (a) CW and (b) XiX decoupling at 80 kHz proton decoupling power. For XiX decoupling, $t_p = 2.6 \times t_r$ was used. This is the same condition as the case of Fig. 4. At 15 kHz sample spinning speed, not only the intensity of the methyl carbon, but also those of other carbons increased about 10% at XiX decoupling compared with CW decoupling. The FWHH of each carbon with XiX decoupling (normalized with those of CW decoupling) at 6 and 15 kHz spinning speeds is summarized in Table 1. This result verified the fact that the efficiency of the XiX decoupling increased by increasing sample mobility.

4. Conclusion

In this section, XiX decoupling is not only effective at high sample spinning speed and high proton decoupling power, but also at moderate sample spinning speed and lower proton decoupling power for mobile samples. For mobile samples, such as rubbers or liquid crystals, T_2 (spin-spin relaxation time) is expected to be long, and the longer data acquisition time with proton decoupling is required for ^{13}C solid state NMR. Long and high power proton decoupling will sometimes damage a probe and change the character of the sample by heat. Therefore, the lower proton decoupling power is required for mobile

samples, however low power CW proton decoupling is not enough to reduce heteronuclear dipolar coupling. Furthermore, there is only one parameter, t_p to be adjusted at XiX decoupling, therefore it is much easier to set up compared with TPPM decoupling. In this manner, low power XiX decoupling is very useful for ^{13}C solid state NMR with mobile samples.

Acknowledgments

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