Fullerene as a Standard Sample for Adjusting the NMR Spectral Resolution in Multiple-Quantum Magic-Angle-Spinning Experiments

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A method using fullerene for adjusting the NMR spectral resolution for multiple quantum magic angle spinning (MQMAS) experiments is proposed. To observe its ^{13}C MAS signal, it is not necessary to apply ^1H decoupling, unavailable with single-resonance MQMAS probes. Although ^{13}C T_1 of fullerene is rather long, a recycle time of 5 s in shimming yields its signal with sufficiently high sensitivity if setting the appropriate Ernst angles corresponding to magnetic fields. It is demonstrated that so-adjusted high resolution is reflected in the ^{87}Rb MQMAS spectra of RbNO_3 .

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Introduction

Spectral resolution is one of the most essential factors in determining the quality of NMR spectra. It is almost self-evident that higher resolution of MQMAS (multiple quantum magic angle spinning) spectra^{1,2} can be obtained, when higher resolution of a standard sample is achieved. Therefore, it is practically important to find a sample that is appropriate for adjusting the spectral resolution.

To observe MQMAS spectra, the strongest possible RF field is required to enhance the multiple-quantum coherence and to avoid spectral distortion.²⁻⁵ For this reason, a special single-resonance probe, instead of a CPMAS double-resonance probe, is desirably utilized. Accordingly, we can not enjoy high-power ^1H decoupling with such a special probe. It follows that a sample containing ^1H nuclei, such as adamantane, is not suitable for adjusting the resolution without ^1H high-power decoupling. In other words, by using the novel sample without containing ^1H nuclei, one can apply the longest possible acquisition time without ^1H decoupling in prolonging the FID by shimming.

We summarize the criteria for such a standard sample with which the spectral resolution is adjusted, as follows:

- (1) No ^1H nuclei should be contained.
- (2) No large quadrupolar interaction should be involved; spin-1/2 nuclei or highly symmetric quadrupolar nuclei should be contained.
- (3) The intrinsic MAS resonance line should be sufficiently sharp.
- (4) The recycle time could be as short as 5 to 10 s and should yield a sufficiently high sensitivity signal with a single transient.
- (5) The sample should be a stable solid at room temperature and pressure.
- (6) The sample should be commercially available at a reasonable cost.

In this article, we show that fullerene (C_{60}) is an appropriate sample for adjusting the spectral resolution; fullerene fulfills all of the above criteria.

Experimental

In the NMR experiments, we used the JEOL ECA/ECX series of NMR spectrometers; the ^1H resonance frequencies were 400, 500, 600, 700, and 930 MHz, and the corresponding magnetic field strengths were 9.4, 11.7, 14.1, 16.4, and 21.9 T. In the case of 14.1 T, the ^{13}C and ^{87}Rb resonance frequencies were 150.9 and 196.4 MHz, respectively. Also, a JEOL single-resonance MQMAS probe was used. All of the NMR experiments were conducted at room temperature and pressure.

We used fullerene to adjust the spectral resolution, or shimming. In the MQMAS experiments, we used RbNO_3 as a test sample to check the MQMAS spectral resolution. Both fullerene and RbNO_3 were purchased from Tokyo Kasei Kogyo and used without further purification.

Results and Discussion

Figure 1 shows the ^{13}C MAS spectra of fullerene at 14.1 T, of which the resolution is adjusted in Fig. 1(a) and not adjusted in Fig. 1(b). The corresponding ^{87}Rb MQMAS spectra of RbNO_3 are shown in Figs. 1(c) and (d), respectively. The linewidth of fullerene is directly reflected in the target MQMAS spectra, as obviously recognized in the F_1 isotropic projections. This shows that adjusting the spectral resolution prior to MQMAS experiments is necessary. The details of the adjustment are discussed and shown below.

The sharpness of the resonance line is required for the sample with which the resolution is adjusted. Table 1 shows the FWHH (full width at half height) of ^{13}C MAS resonance lines of fullerene at various sample spinning frequencies at 14.1 T, which we realized through elaborate shimming; the values of the FWHH indicate the highest possible resolution that we

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Fig. 1 ^{13}C MAS spectra of fullerene at a spinning frequency of 5 kHz with which the spectral resolution is adjusted up to FWHH of 3.3 Hz (a), and not adjusted and having FWHH of 170 Hz. Under these ^{13}C resolution, or the shimming conditions, the ^{87}Rb MQMAS spectra of RbNO_3 are observed at a spinning frequency of 19 kHz and shown in (c) and (d), respectively. F_1 isotropic projections of the individual 2D spectra reflect the inhomogeneity of magnetic fields represented by ^{13}C resolution shown in Figs. 1(a) and (b).

achieved. Once the sample is spun, the resonance line becomes sharp from 200 to 2 Hz. Although further line narrowing may be expected at faster spinning frequencies, 5 kHz is experimentally found to be sufficient, as shown in Fig. 1 and Table 1.

As a sample with which the resolution is adjusted, one of the criteria is a comparatively short T_1 relaxation time for a fast recycle delay. Table 2 gives the ^{13}C T_1 values of fullerene obtained at various magnetic fields (B_0) from 9.4 to 21.9 T. Obviously, a higher magnetic field makes the relaxation time (T_1) shorter, in contrast to the ordinary rigid solid samples. From Table 2, we can judge that the signal of fullerene is more easily acquired at a higher magnetic field. It is reported⁶⁻⁹ that the T_1 relaxation of fullerene at room temperature is dominated by the chemical-shift anisotropy, and the value of T_1 is consequently proportional to $1/B_0^2$, which elucidates our observation.

The T_1 value of 25 s at a high field of 14.1 T is still long for the recycle delay of shimming. However, the combination of faster recycle delays and small flip angles can optimize the experimental condition. For example, if the recycle delay is fixed at 5 s, the Ernst angles¹⁰ for the individual magnetic fields are evaluated as in Table 3; the sensitivity of the ^{13}C signal intensity is 31.6% compared with that of the almost completely recovered signal using a 90 degree pulse after 125 s, 5-times that of T_1 . This sensitivity is sufficiently high, and we can repeat the shimming with a recycle delay of 5 s. In fact, the resolution is adjusted so as to obtain the spectrum shown in Fig. 1(a).

Also, the relative sensitivities of fullerene at the above-mentioned various magnetic fields normalized with the signal intensity at 14.1 T are given in Table 3. A higher magnetic field makes the signal sensitivity higher, partly because of a shorter relaxation time (T_1). However, even at a low field of 9.4 T, more than 50% of the sensitivity compared with that at 14.1 T is expected, which indicates that fullerene can still be used for shimming.

When MQMAS probes are not available, prevailing CPMAS double-resonance probes ordinarily equipped may instead be

Table 1 Linewidth (FWHH) of the ^{13}C MAS resonance line of fullerene at various sample spinning frequencies, ν_R observed at 14.1 T

ν_R/kHz	FWHH/Hz
15	1.5
10	1.9
5	2.0
0	200

Table 2 ^{13}C longitudinal relaxation time (T_1) of fullerene at various magnetic fields, B_0 T (ν_0 MHz for ^1H Larmor frequencies)

B_0/T (ν_0/MHz)	T_1/s
9.4 (400)	50
11.7 (500)	30
14.1 (600)	25
16.4 (700)	20
21.9 (930)	13.3

Table 3 Ernst angles (θ_{EA} degree) in the case of a recycle time of 5 s at various magnetic fields, B_0 T (ν_0 MHz for ^1H Larmor frequencies), and the sensitivities relative to the full recovery after five times of T_1 at each field, $(S/N)_{\text{EA}}/(S/N)_{\text{FR}}$

B_0/T (ν_0/MHz)	$\theta_{\text{EA}}/\text{degree}$	$(S/N)_{\text{EA}}/(S/N)_{\text{FR}}, \%$	$(S/N)_{\text{EA}}/(S/N)_{\text{EA}@14.1}, \%$
9.4 (400)	25.2	22.2	54.4
11.7 (500)	32.2	28.8	75.6
14.1 (600)	35	31.6	100
16.4 (700)	38.8	35.3	125.4
21.9 (930)	46.6	43.1	193.6

The relative sensitivities normalized with that for 14.1 T, $(S/N)_{\text{EA}}/(S/N)_{\text{EA}@14.1}\%$ are shown, for which the sensitivities are assumed to be proportional to $B_0^{3/2}$.

utilized for MQMAS experiments. Even in that case, adjustment of the spectral resolution using fullerene is favorably applicable. Although high-power ^1H decoupling can be applied during shimming for samples containing ^1H nuclei, long decoupling necessary to achieve high spectral resolution might damage to the probe and other equipment.

We dare to point out the unfavorable aspects of fullerene, such as its lower sensitivity at lower magnetic fields and a slightly high cost of 400 US dollars per 1 g, although it is commercially available with ease.

Conclusions

In this article, it is demonstrated that fullerene is useful for the adjusting the spectral resolution for MQMAS experiments; ^1H decoupling is irrelevant to observe its ^{13}C signal, and so shimming can be performed using single-resonance MQMAS probes. There is no risk to damage probes and other equipment, caused by long high-power decoupling pulses. We can enjoy an acquisition time as long as necessary. The intrinsic ^{13}C MAS resonance line of fullerene is found to be sharp enough to adjust shimming. Indeed, the relaxation time (T_1) of fullerene is long,

but it becomes possible to shim at every 5 s with sufficiently high signal sensitivity if the appropriate Ernst angle is applied.

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