Chemical Physics Letters 678 (2017) 265–270

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Cryocoil magic-angle-spinning solid-state nuclear magnetic resonance probe system utilized for sensitivity enhancement in multiple-quantum magic-angle-spinning spectroscopy for a low-γ quadrupolar nucleus of ^{85}Rb

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ARTICLE INFO

Article history:
Received 17 January 2017
In final form 21 April 2017
Available online 23 April 2017

Keywords:
Cryocoil MAS
Solid-state NMR
MQMAS
Low-γ nuclei
Sensitivity enhancement
Signal-to-noise ratio (SNR)
^{85}Rb
Quadrupolar nuclei
Cryogenic temperature (CT)
Room temperature (RT)

ABSTRACT

Sensitivity enhancement in solid-state nuclear magnetic resonance using a cryocoil magic-angle-spinning system was investigated, by comparing, at room temperature and at cryogenic temperature, the signal-to-noise ratios of the multiple-quantum magic-angle-spinning spectra as well as the conventional spectra for a low-γ nucleus ^{85}Rb in $RbNO_3$. The increase of the sample-coil quality-factor and the thermal noise reduction were found to enhance the sensitivities by approximately 4.5 times; the former yielded the further doubled signal increase in the multiple-quantum spectroscopy via the increase of the radio-frequency field strengths. Eventually, 20–30 times of the sensitivity enhancement were realized in the two-dimensional multiple-quantum magic-angle-spinning spectra.

1. Introduction

High-resolution solid-state nuclear magnetic resonance (NMR) spectroscopy is widely used for characterizing molecular and crystallographic structures of organic and inorganic materials [1–5]; magic-angle-spinning (MAS) techniques usually incorporated to achieve high resolution for easily available powdered samples, eliminating spectral broadenings caused by chemical-shift anisotropies, internuclear dipolar couplings, and so on. The most conspicuous feature of the method is to yield microscopic information of materials as they are, and without necessity of chemical manipulation such as dissolution, melting, and adding any other materials. On the other hand, low spectral sensitivity in solid-state NMR is a persistent subject, originating from broad resonance lines compared with those in solution-state NMR. Thus far, several approaches have been attempted to develop NMR hardware realizing sensitivity enhancement, succeeding in providing practicable characterization means in chemistry and materials science. The use of ultra-high-field magnets over 20 T [6] is a straightforward way to increase NMR sensitivity, although the construction and the maintenance of such magnets may be costly. Another obvious remedy for low sensitivity is the use of large-volume sample containers or MAS rotors, which may suffer from slow spinning and low radio-frequency (*rf*) field strength, far from optimal in some experiments. Dynamic nuclear polarization (DNP) combined with MAS [7–10] has been reported as a prospective technique of sensitivity enhancement, where samples should, however, be doped with radicals and be placed at an extremely low temperature.

As an alternative way for sensitivity enhancement, we have developed cryocoil MAS NMR probe systems [11–15]; albeit an MAS-rotating sample placed at room temperature, a sample coil and a preamplifier are cooled down to extremely low temperatures, increasing signal intensities via the increase of the

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http://dx.doi.org/10.1016/j.cplett.2017.04.073
0009-2614/

sample-coil quality-factor (Q-factor) as well as decreasing thermal noises. In the present work, we report an application of cryocoil MAS NMR to multiple-quantum MAS (MQMAS) spectroscopy [16,17] of a low-γ nucleus of ^{85}Rb (I = 5/2), having small gyromagnetic ratios γ. MQMAS yields isotropic and high-resolution resonance lines in one spectral dimension and anisotropic powder patterns in the other dimension, unraveling overlapped patterns, for half-integer quadrupolar nuclear spins, utilizing indirect observation of multiple-quantum coherences, much less intense compared with the conventional single-quantum coherences. Also, low-γ nuclei are worth attempting to apply cryocoil MAS since their receptivities become lower in proportional to the cube of γ [1,18]. We illustrate how NMR sensitivities are enhanced, by comparing the experimental results, in which we set the detection system of the cryocoil MAS probe at room temperature ($T_c \sim 298$ K) defined as 'RT' condition, and set that at cryogenic temperature ($T_c < 20$ K) defined as 'CT' condition as shown below, where T_c is the temperature of the sample coil.

2. Experimental

Our cryocoil MAS probe system consists of a probe, a refrigerator, and a circulator. Cold helium gas flows from the refrigerator to the probe, cooling the sample coil attached to a heat exchanger made of a sapphire block at T_c = 17 K and then the embedded preamplifier and duplexer at 50 K, helium gas is recycled with a closed-cycle refrigerating system [14]. The sample coil in the probe is composed of ribbon-solenoid one plated on the sapphire block, the in-diameter of which is 6.7 mm. The sample container, or the MAS rotor, has the out-diameter of 4 mm, the length of 22.5 mm, and the volume of 50 μl. The maximum MAS speed is 18 kHz. The probe fits to widebore superconducting magnets, and the MAS rotor can be loaded into and exported from the probe retained in the magnet through a top-loading attachment. The magic angle can be adjusted by inclining the probe against the magnet using an adjusting screw with the accuracy of ±0.4 deg. The static magnetic field B_0 is 9.4 T (^{1}H resonance frequency is 400 MHz), and the probe tunable range is from 24 to 72 MHz, covering a wide variety of low-γ nucleus resonance frequencies such as ^{25}Mg (24.5 MHz), ^{137}Ba (44.4 MHz), and ^{171}Yb (70.0 MHz) [1,18], though the probe is single tuned.

An NMR spectrometer of ECA400 from JEOL RESONANCE Inc. was used, controlled with Delta software; data analyses such as signal-to-noise ratio (SNR) calculations were also done with Delta. Pulse programs of spin-echo and MQMAS sequences pre-installed in Delta were utilized to obtain conventional single-quantum spectra and MQMAS spectra, respectively, the latter sequence of which was modified to add a spin-echo subsequence block. The MQMAS pulse sequence consists of three pulses, apart from the additional spin-echo pulse, an excite pulse for triple-quantum coherences, a conversion pulse for them to single-quantum coherences, and a z-filter soft pulse, yielding pure-absorptive two-dimensional MQMAS spectra [19–23].

A sample of $RbNO_3$ was chosen to demonstrate low-γ nucleus MQMAS experiments for ^{85}Rb (38.6 MHz); the receptivity of ^{85}Rb with respect to ^{13}C is 43.0, much smaller than 277 of ^{87}Rb (130.8 MHz) [18], for which MQMAS spectra were frequently reported using $RbNO_3$ [19,22,24–28]. The sample weight of $RbNO_3$ loaded in the MAS rotor was 90.5 mg. The MAS speed was 15 kHz. The *rf* field strengths ν_{rf} were evaluated from the ^{85}Rb nutation signals of RbCl in solids. ^{85}Rb chemical shifts are referenced to the RbCl resonance line. The magic angle was adjusted using ^{35}Cl (39.2 MHz) spinning-sideband intensities of NaCl. All the samples were purchased from Aldrich and used without further purification.

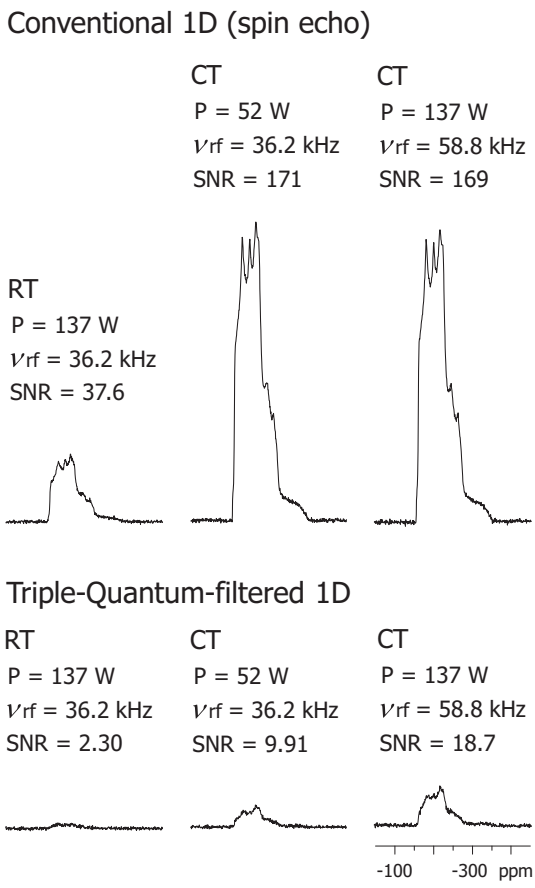

Fig. 1. Comparison of one-dimensional (1D) ^{85}Rb MAS NMR spectra of $RbNO_3$ in conventional spin-echo and triple-quantum-filtered experiments with the *rf* field strengths ν_{rf} of 36.2 and 58.8 kHz at room temperature (RT) and cryogenic temperature (CT); the increase of sample-coil Q-factor from RT to CT renders the *rf* field strengths ν_{rf} enhance from 36.2 to 58.8 kHz with the identical probe-in power P of 137 W, and the CT experiments with P = 52 W and ν_{rf} = 36.2 kHz were performed for comparison. Triple-quantum-filtered spectra were obtained using a two-dimensional (2D) MQMAS pulse sequence with the evolution period fixed to t_1 = 0. For all the experiments, the signal accumulation was 15 360 with a recycle delay of 0.1 s and an acquisition time of 17 ms, the accumulation time being *ca* 30 min. No line broadening function was applied. The pulse conditions for the individual *rf* field strengths were optimized to maximize the signals at CT and employed to the RT experiments; the echo time 600 μs was used.

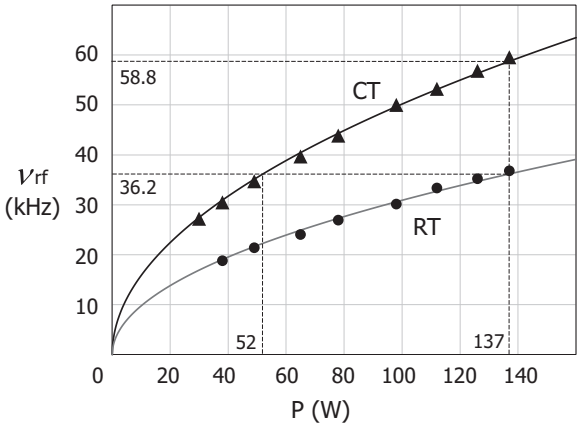

Fig. 2. *rf* field strengths ν_{rf} for the given values of the probe-in power P at RT (circles) and CT (triangles), evaluated from the ^{85}Rb nutation signals of RbCl in solids. It was found that ν_{rf}(RT) (in kHz) = 3.09 $\sqrt{P(\text{in W})}$ and ν_{rf}(CT) (in kHz) = 5.02 $\sqrt{P(\text{in W})}$ in the observed range of P, leading to the gain ν_{rf} (CT)/ν_{rf} (RT) of 1.62.