

# Long-term stability of rotor-controlled MAS frequencies to 0.1 Hz proved by $^{14}\text{N}$ MAS NMR experiments and simulations

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## Abstract

Experimental and simulated  $^{14}\text{N}$  MAS NMR spectra of the  $\text{NH}_4^+$  ions in the two polymorphs, *mS60* and *mP60*, of  $(\text{NH}_4)_2\text{MoO}_4$  are used to illustrate that a long-term stability of rotor-controlled MAS frequencies to 0.1 Hz can be achieved using commercial instrumentation (MAS speed controller and 7.5 mm MAS probe with a single marked rotor) attached to a highly pressure-stabilized air supply. A new modification of the STARS simulation software employs a Gaussian distribution for the experimental spinning frequency around the frequency set for the MAS speed controller. A simulated spectrum is then obtained by summation of several calculated spectra for evenly spaced spinning frequencies around the set frequency with relative weight factors corresponding to the Gaussian distribution. © 2006 Elsevier Inc. All rights reserved.

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## 1. Introduction

In the course of our continuous efforts to advance solid-state  $^{14}\text{N}$  MAS NMR spectroscopy [1], a number of basic, but significant experimental requirements important for securing an optimum outcome of the measurements have been encountered and remedied. These include (i) determination of the optimum/correct length for the rf cable between the probe and preamplifier to minimize the effect of phase glitches (which may cause severe tilting of the spinning sideband (ssb) intensities across the spectra), thereby ensuring a decent rf-offset appearance of the spectra; (ii) construction of alternative hardware to low-/band-pass filters in the probe observe line, when  $^1\text{H}$  decoupling is mandatory, since such filters cause significant intensity suppression in the wings of the ssbs for low- $\gamma$  nuclei [2]; (iii) precise adjustment of the magic-angle ( $54.736^\circ$ ) to

within a few thousands of a degree ( $< \pm 0.003^\circ$ ) [1]; and (iv) a long-term high stability for the spinning frequency of about 0.1 Hz [1]. We have generally claimed that the  $^{14}\text{N}$  MAS NMR spectra presented by our group have been acquired with a long-term spinning stability better than 0.1–0.3 Hz [1,3] as judged from the extremely well-resolved lineshapes and/or identical linewidths for the several hundreds of ssbs observed across the spectra for many of the different samples investigated. On several occasions at oral or poster presentations, this high degree of spinning stability has been questioned with arguments of great controversy and comments such as “in rotor-controlled MAS the spinning stability can not be better than  $\pm 1$  Hz which is the optimum resolution of the frequency counter per second”. Thus, the actual sampling time (30 ms) and clock frequency (2.0 MHz) used by the MAS speed controller have not been taken into account in these arguments. It is the simple combination of the excellent timing of a commercial MAS speed controller with our original mechanical pressure stabilization of the air-supply source which

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has led to the claimed very high long-term spinning stability. Pressure stabilization of the air supply using three large ballast tanks (60, 60, and 45 gallon) combined with multiple marking of the rotor has earlier been shown to improve spinning-speed stability [4]. A simple homemade and stand-alone MAS speed controller has recently been described for which five evenly spaced marks on a 7.5 mm rotor provide spinning-frequency control to within  $\pm 0.2$  Hz [5]. Ten evenly spaced marks are quoted to give a precision of  $\pm 0.1$  Hz. Accordingly, this design and the presented experimental spectral results correspond to a single space-marked 7.5 mm rotor exhibiting a MAS-frequency stability of 1 Hz, thereby conforming to the comment quoted above.

In this communication we present full justification for our claim that long-term MAS spinning stability of 0.1 Hz is feasible using a commercially available MAS speed controller and a commercially available 7.5 mm rotor with only a single laser mark, when combined with our highly pressure-stabilized air supply. This high degree of spinning stability, employing commercially available equipment, would be welcome in most solid-state MAS NMR experiments, in particular for ordinary MAS NMR spectra of the satellite transitions [1], rotor-synchronized experiments, and the various versions of satellite transition (ST) MAS NMR [6–8] of quadrupolar nuclei, to mention just a few. The claimed long-term spinning stability of 0.1 Hz will be shown by comparison of the recent experimental  $^{14}\text{N}$  MAS NMR “fingerprint” spectra for the two polymorphs, *mS60* and *mP60*, of  $(\text{NH}_4)_2\text{MoO}_4$  [9] with the present unique experimental spectra and simulations, based on the actual optimized spectral and instrumental parameters.

## 2. Experimental

The samples of the *mS60* and *mP60* polymorphs of  $(\text{NH}_4)_2\text{MoO}_4$  used here were obtained as described in a recent investigation [9], i.e., the *mS60* polymorph was synthesized according to the procedure by Dittmann and Schweda [10], while the *mP60* polymorph was obtained from Aldrich.

Before describing the NMR instrumentation employed, we shall shortly present the original installations used for purification and pressure stabilization of the air source for the MAS speed controller; these have been prerequisites for our advancements within  $^{14}\text{N}$  MAS NMR spectroscopy [1–3]. Compressed air from a large departmental air compressor, with water and oil being partly removed, is passed through two filters of active carbon and a particle filter at the site of the NMR spectrometers to remove residual oil and dust particles. It is then dried to a dew point of about  $-100$  °C by passage through either of two large zeolite-filled towers (150 cm height  $\times$  13 cm o.d.), which in turns are automatically regenerated every 8 h and thus, always provide extremely dry air (occasionally checked for  $\text{H}_2\text{O}$  by FTIR). As outlined in Fig. 1, the clean, compressed

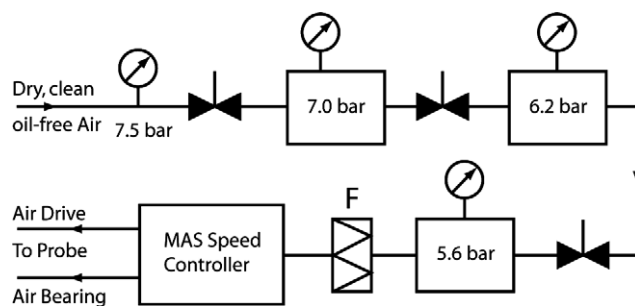


Fig. 1. Schematic diagram showing the installation used to eliminate the variation in air pressure from a large central air compressor, before the air is supplied to a MAS speed controller in solid-state MAS NMR experiments (see text). Upon entry to each of the three 10 L ballast tanks the air pressure is reduced by approximately 0.6 bar from one ballast tank to the next using standard pressure regulators placed in front of each tank. Before entering the MAS speed controller, a particle filter (F) serves as a protection against possible particles released from the zeolite drying towers or ballast tanks.

air (7.5 bar) enters three in-series 10 L ballast tanks, in front of which regulators are used to reduce the pressure by approximately 0.6 bar from one tank to the next, and which are all placed outside the NMR lab about 5 m from the MAS speed controller. The purpose of the three ballast tanks is to minimize variations in the pressure of the air supply entering the controller. Otherwise, this pressure would vary significantly according to the large departmental compressor tanks being pressurized/depressurized, and this would obviously influence the precision of the speed control. Finally, just before entering the MAS speed controller the clean, pressure-stabilized air is passed through a second particle filter.

The  $^{14}\text{N}$  MAS NMR experiments were performed as described recently for the same two polymorphs [9], except for the slight degradation in the stability of the spinning frequency to about 1 Hz, as will be described below. Thus, the  $^{14}\text{N}$  MAS spectra were recorded at 43.33 MHz on a Varian Unity INOVA-600 spectrometer equipped with a 14.1 T widebore magnet. A Varian/Chemagnetics broadband low- $\gamma$  ( $\leq ^{13}\text{C}$ ) frequency 7.5 mm T3<sup>®</sup> CP/MAS probe, based on transmission-line-tuning technology, was used. The spinning frequency employed ( $\nu_r = 1500$  Hz) was stabilized using the commercially available Chemagnetics “MAS Speed Controller”. Most importantly it is emphasized that the commercial Chemagnetics 7.5 mm o.d. pencil rotors were used as received with only a single laser mark, i.e., no multiple evenly spaced marks on the rotors were employed.

The spectra were analyzed using the STARS solid-state NMR software package as also described recently for the *mS60* and *mP60* polymorphs of  $(\text{NH}_4)_2\text{MoO}_4$  [9]. However, in order to correctly simulate the  $^{14}\text{N}$  MAS NMR spectra obtained in this work, the STARS program was modified to cope with instabilities in spinning frequencies as described in the section below. Otherwise, the conventions employed for the interaction parameters and other

parameters in STARS are identical to those described earlier [1–3,9].

### 3. Results and discussion

The very characteristic  $^{14}\text{N}$  MAS NMR “fingerprint” spectra, recently studied for the two polymorphs *mS60* and *mP60* of  $(\text{NH}_4)_2\text{MoO}_4$  [9], along with their transformation products for  $\nu_r = 1500$  Hz and for some ammonium polymolybdates, serve as excellent samples for demonstrating the claimed long-term spinning stability of 0.1 Hz due to the narrow linewidths of about 25 Hz for the ssbs. Precise values for the  $^{14}\text{N}$  quadrupole coupling and chemical shift parameters for the *mS60* and *mP60* polymorphs were obtained previously [9]. Most recently, in relation to extended studies of the ammonium monomolybdates, it therefore came as somewhat of a surprise when a quite different  $^{14}\text{N}$  MAS NMR spectrum of the *mS60* polymorph was obtained for the same spinning frequency  $\nu_r = 1500$  Hz as before (Fig. 2b). Considering the appearances of the

widely different  $^{14}\text{N}$  MAS NMR spectra observed for the transformation products of the *mS60* and *mP60*  $(\text{NH}_4)_2\text{MoO}_4$  polymorphs [9], the first idea that came to mind was: Does this spectrum reflect yet another transformation product for  $(\text{NH}_4)_2\text{MoO}_4$ ? However, it appeared impossible to achieve a decent visual agreement between the experimental spectrum and a fit based on this spectrum which contains two well-resolved resonances in the isotropic region identical to the two isotropic resonances reported for the *mS60* polymorph [9]. Thus, it was decided to observe if a similar change has occurred for the  $^{14}\text{N}$  MAS NMR spectrum of the *mP60* polymorph. This  $^{14}\text{N}$  MAS NMR spectrum ( $\nu_r = 1500$  Hz) also appears (Fig. 3b) very different from that recently reported for the same sample at  $\nu_r = 1500$  Hz [9]. It was not possible to achieve a satisfactory visual agreement for a fit to this spectrum either. Clearly, this indicated that yet another instrumental parameter (similar to that of the effect of cable lengths, or “overcoupling” of the probe-Q by rf high-band low-/band-pass filters in the observe line

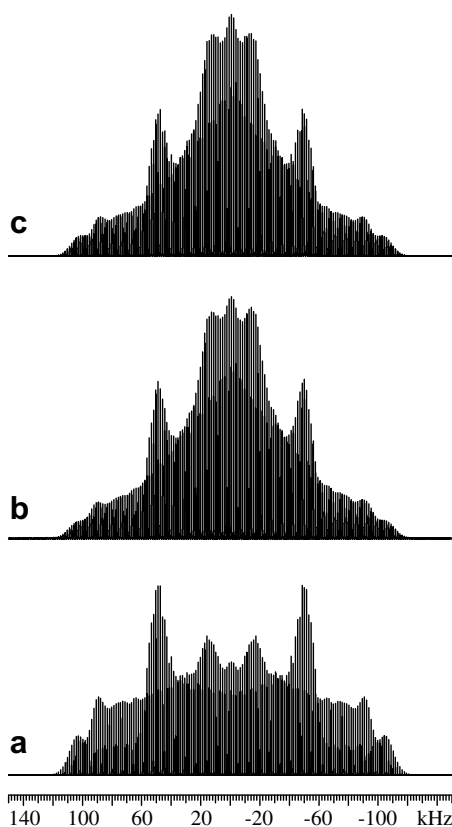


Fig. 2. Experimental (b) and simulated (a and c)  $^{14}\text{N}$  MAS NMR spectra (43.33 MHz at 14.1 T) of the *mS60* polymorph of  $(\text{NH}_4)_2\text{MoO}_4$ , which illustrate the effect of an instability ( $\Delta\nu_r$ ) in spinning frequency ( $\nu_r$ ) of 1.1 Hz. (a) Simulated spectrum corresponding to the parameters in Table 1 for the two  $\text{NH}_4^+$  sites (1:0.85), no jitter ( $\Delta\nu_r = 0.0$  Hz) in the spinning frequency  $\nu_r = 1500$  Hz, and a deviation from exact magic-angle setting of  $\Delta\theta = -0.003^\circ$ . (b) Experimental spectrum acquired for  $\nu_r = 1500$  Hz, 40000 scans, and a relaxation delay of 2 s. (c) Simulated spectrum corresponding to the parameters (Table 1) determined from an iterative fit to the experimental spectrum in (b) using  $\Delta\nu_r = 1.1$  Hz (cf Fig. 4).

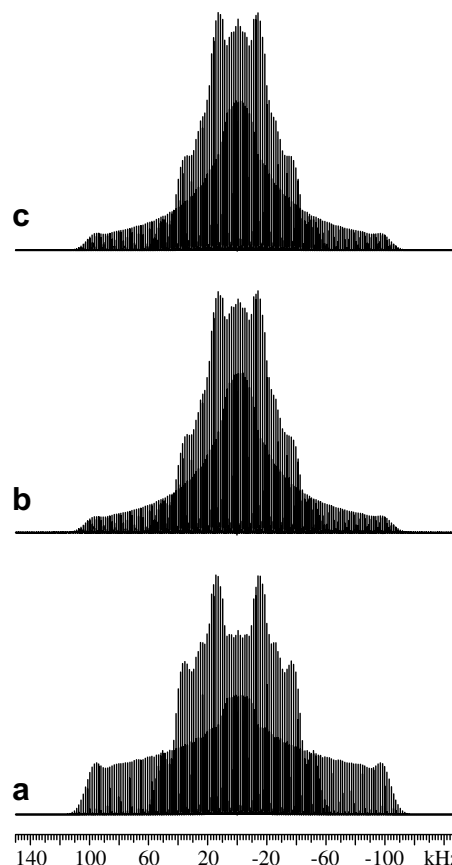


Fig. 3. Experimental (b) and simulated (a and c)  $^{14}\text{N}$  MAS NMR spectra (43.33 MHz at 14.1 T) of the *mP60* polymorph of  $(\text{NH}_4)_2\text{MoO}_4$ . (a) Simulated spectrum corresponding to the parameters in Table 1 for the two  $\text{NH}_4^+$  sites (1:1), no jitter ( $\Delta\nu_r = 0.0$  Hz) for  $\nu_r = 1500$  Hz, and a deviation from exact magic-angle setting of  $\Delta\theta = -0.001^\circ$ . (b) Experimental spectrum acquired for  $\nu_r = 1500$  Hz, 31000 scans, and a relaxation delay of 2 s. (c) Simulated spectrum corresponding to the parameters (Table 1) determined from an iterative fit to the experimental spectrum in (b) using  $\Delta\nu_r = 0.9$  Hz.

between the preamp and probe) may affect the appearance of the experimental spectrum. In fact, measurements of linewidths for the spinning sidebands (ssbs) throughout the full width of the spectra showed a continuous increase in the linewidths for the ssbs towards the wings of the spectra. This indicated that a jitter in the spinning frequency could be the cause for the somewhat strange appearances of the spectra in Figs. 2b and 3b. Indeed, cleaning the ends of the fibre optics cables within the stator, using isopropanol, followed by re-recording of the  $^{14}\text{N}$  MAS NMR spectra for both samples resulted in appearances similar to the experimental spectra recently reported for these samples [9] and to the simulated spectra in Figs. 2a and 3a. It is noted that in fitting to experimental ssb spectra employing integrated intensities of the ssbs, as opposed to lineshapes of the ssbs, a jitter in spinning frequency becomes less important.

To further investigate the reason for the unusual appearances of the experimental spectra in Figs. 2b and 3b and to confirm/determine the magnitude of the proposed jitter in spinning frequency, it was decided to introduce a modification to our STARS simulation software. In the standard version of STARS the frequency of the  $n$ th ssb, resulting from a MAS NMR experiment, is assumed to be a multiplet  $n$  of the spinning frequency ( $\nu_r$ ) used by the MAS speed controller. In the new, modified version of STARS, the experimental spinning frequency is assumed to have a Gaussian distribution around  $\nu_r$  with a Gaussian width (standard deviation,  $\Delta\nu_r$ ) characterizing the stability/jitter; i.e., the spinning frequency is in the range ( $\nu_r - \Delta\nu_r$ ,  $\nu_r + \Delta\nu_r$ ) 68% of the time and in the range ( $\nu_r - 2\Delta\nu_r$ ,  $\nu_r + 2\Delta\nu_r$ ) 95% of the time. Thus, a simulated spectrum is obtained by performing several calculations employing spinning frequencies evenly distributed in the range ( $\nu_r - 2\Delta\nu_r$ ,  $\nu_r + 2\Delta\nu_r$ ) and followed by coaddition of the calculated spectra with relative weight factors corresponding to the Gaussian distribution.

In order to observe the effect of a possible jitter in spinning frequency on the appearances of the  $^{14}\text{N}$  MAS NMR spectra for the *mS60* and *mP60* polymorphs of  $(\text{NH}_4)_2\text{MoO}_4$  a series of simulated spectra, employing the modified STARS software, the spectral parameters ( $C_Q$ ,  $\eta_Q$ , and  $\delta_{\text{iso}}$ ) recently reported for the two polymorphs [9], and selected jitter values (i.e.,  $\Delta\nu_r$  in the range 0–2 Hz) in  $\nu_r$ , have been performed for  $\nu_r = 1500$  Hz. From these simulated spectra, some of which are presented in Fig. 4, it is evident that jitter in  $\nu_r$  is indeed responsible for the unusual appearances of the experimental spectra for the *mS60* and *mP60* polymorphs in Figs. 2b and 3b, respectively. Furthermore, a jitter in the spinning frequency ( $\nu_r = 1500$  Hz) of  $\Delta\nu_r = 1.1$  Hz (*mS60*, Fig. 2b) and  $\Delta\nu_r = 0.9$  Hz (*mP60*, Fig. 3b) could be determined for the two samples from these simulations. Introducing these jitter values in the STARS software now allows iterative optimizations of the experimental spectra in Figs. 2b and 3b to be performed to perfection. The resulting spectral parameters ( $C_Q$ ,  $\eta_Q$ , and  $\delta_{\text{iso}}$ ) are summarized in Table 1 and the corresponding simulated

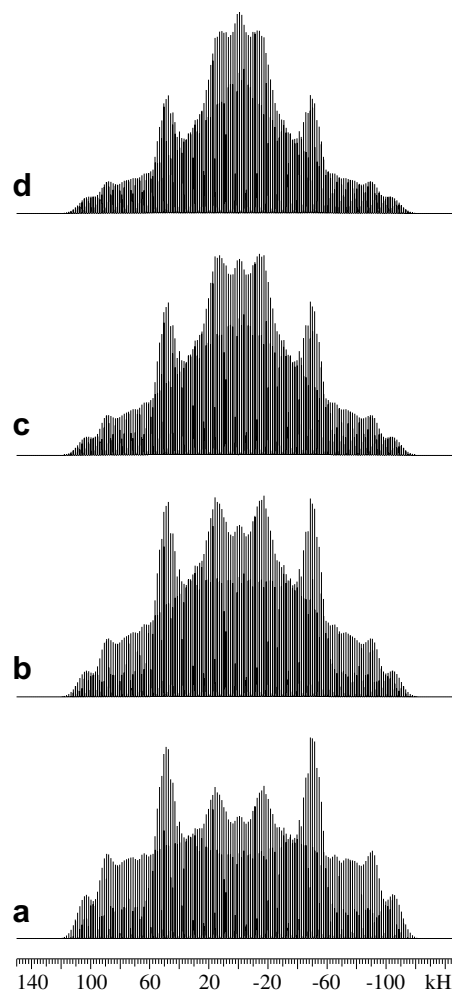


Fig. 4. Simulated  $^{14}\text{N}$  MAS NMR spectra (a–d) for the *mS60* polymorph of  $(\text{NH}_4)_2\text{MoO}_4$ , illustrating the effect of small changes in  $\Delta\nu_r$  on the appearance of the spectra, (a)  $\Delta\nu_r = 0.0$  Hz, (b)  $\Delta\nu_r = 0.4$  Hz, (c)  $\Delta\nu_r = 0.8$  Hz, and (d)  $\Delta\nu_r = 1.2$  Hz. The simulations employed the parameters listed in Table 1 for the two  $\text{NH}_4^+$  sites (1:0.85),  $\nu_r = 1500$  Hz, a deviation from exact magic-angle setting of  $\Delta\theta = -0.003^\circ$ , and 17 simulated spectra for the Gaussian distribution in  $\nu_r$  (see text).

Table 1

$^{14}\text{N}$  isotropic chemical shift ( $\delta_{\text{iso}}$ ) and quadrupolar coupling parameters ( $C_Q$ ,  $\eta_Q$ ) determined from  $^{14}\text{N}$  MAS NMR spectra exhibiting a jitter of  $\Delta\nu_r = 0.9$  Hz and  $\Delta\nu_r = 1.1$  Hz in the spinning frequency  $\nu_r = 1500$  Hz for the *mS60* and *mP60* polymorphs of  $(\text{NH}_4)_2\text{MoO}_4$ , respectively<sup>a</sup>

Compound	Sites	$\delta_{\text{iso}}$ (ppm)	$C_Q$ (kHz)	$\eta_Q$
$(\text{NH}_4)_2\text{MoO}_4$ <i>mS60</i>	N(1)	-17.4	144.6	0.09
	N(2)	-20.5	151.2	0.71
$(\text{NH}_4)_2\text{MoO}_4$ <i>mP60</i>	N(1)	-22.2	144.8	0.90
	N(2)	-16.6	77.8	0.49

<sup>a</sup> The  $\delta_{\text{iso}}$  values (relative to an external sample of solid  $\text{NH}_4\text{Cl}$ ) have an error limit of  $\pm 0.1$  ppm and include corrections for the second-order quadrupolar shifts. The  $C_Q$  values have error limits better than  $\pm 3$  kHz and the error limits for  $\eta_Q$  are better than  $\pm 0.03$ .

spectra are presented in Figs. 2c and 3c for the jitter values  $\Delta\nu_r = 1.1$  and 0.9 Hz, respectively. Excellent agreements are observed between the experimental spectra (Figs. 2b and

3b) and the optimized simulations (Figs. 2c and 3c). Similarly, the  $C_Q$ ,  $\eta_Q$ , and  $\delta_{\text{iso}}$  values (Table 1) determined from iterative fitting to the experimental spectra are in perfect agreement (well within error limits) with the data recently determined from their so-called “fingerprint” spectra [9]. Simulated spectra for the *mS60* and *mP60* polymorphs using the parameters listed in Table 1, but without introducing any jitter in  $\nu_r$  (=1500 Hz), are shown in Figs. 2a and 3a. These spectra are in excellent agreement with the recently published experimental and simulated spectra assuming no jitter in  $\nu_r$  (=1500 Hz) [9]. From comparison of these experimental spectra with the series of simulated spectra including a variety of jitter values ( $\Delta\nu_r$ ) it can be judged that the long-term spinning stability for the recently recorded  $^{14}\text{N}$  MAS NMR spectra of the *mS60* and *mP60* polymorphs [9] is 0.1 Hz; generally we find  $\Delta\nu_r$  in the range 0.1–0.2 Hz. This is in full agreement with the same high degree of spinning stability claimed in our earlier  $^{14}\text{N}$  MAS NMR studies [1,2] based on linewidths of the ssbs in particular for nitrate ions, but without the experimental proof reported here. The observed long-term spinning stability of 0.1 Hz for a single marked rotor is in accordance with the fact that the Chemagnetics MAS speed controller samples for 30 ms and yields a 1 Hz frequency resolution at a spinning frequency of 33.3 kHz; i.e., a 0.1 Hz frequency resolution could be expected at 3333 Hz. Finally, it should be noted that for spinning frequencies higher than  $\nu_r = 1500$  Hz, e.g. >10 kHz employing smaller rotor sizes than the 7.5 mm o.d. used here, a slight degradation in the spinning stability is expected for the abovementioned feature of the MAS speed controller, but also because the smaller rotors are more susceptible to any change (e.g., by regulation) in the air-drive flow. However, for  $\nu_r = 7.0$  kHz (7.5 mm o.d. rotor) and  $\nu_r = 12.0$  kHz (5.0 mm o.d. rotor), we have earlier reported spinning stabilities of <0.5 Hz [1] and <1.0 Hz [2], respectively, as determined from the linewidths for the ssbs across the manifold of ssbs and for single marked rotors.

In conclusion, from actual  $^{14}\text{N}$  MAS NMR experiments, this study has shown that long-term spinning stability on the order of 0.1 Hz can be achieved for a single laser marked 7.5 mm o.d. rotor using a commercial MAS speed controller and a highly pressure-stabilized air supply. For multiple evenly spaced marks on the rotor a still higher degree of spinning stability may be possible. Furthermore, it is demonstrated (and one should be aware) that so-called “fingerprint” MAS NMR spectra can show dramatic changes for spinning instabilities of only about 1 Hz. Incorporation of a Gaussian distribution describing the instabil-

ity in spinning frequency into a simulation software program allows simulation of such spectra and at the same time determination of the jitter in spinning frequency.

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