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Technical aspects of fast magic-angle turning NMR for dilute spin-1/2 nuclei with broad spectra

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ABSTRACT

For obtaining sideband-free spectra of high-Z spin-1/2 nuclei with large (>1000 ppm) chemical-shift anisotropies and broad isotropic-shift dispersion, we recently identified Gan's modified five-pulse magic-angle turning (MAT) experiment as the best available broadband pulse sequence, and adapted it to fast magic-angle spinning. Here, we discuss technical aspects such as pulse timings that compensate for off-resonance effects and are suitable for large CSAs over a range of $1.8\gamma B_1$; methods to minimize the duration of z-periods by cyclic decrementation; shearing without digitization artifacts, by sharing between channels (points); and maximizing the sensitivity by echo-matched full-Gaussian filtering. The method is demonstrated on a model sample of mixed amino acids and its large bandwidth is highlighted by comparison with the multiple-π-pulse PASS technique. Applications to various tellurides are shown; these include GeTe, Sb_2Te_3 and $Ag_{0.53}Pb_{18}Sb_{1.2}Te_{20}$, with spectra spanning up to 190 kHz, at 22 kHz MAS. We have also determined the ^{125}Te chemical shift anisotropies from the intensities of the spinning sidebands resolved by isotropic-shift separation.

1. Introduction

Magic-angle spinning NMR spectra of high-Z nuclei such as ^{125}Te, ^{207}Pb, ^{119}Sn, and ^{113}Cd in non-cubic environments are often crowded with spinning sidebands overlapped with the peaks at the isotropic shifts over a broad spectral range; this overlap interferes with the determination of isotropic chemical and Knight shifts, and evaluation of chemical shift anisotropies. Most methods designed for suppressing sidebands [1,2] employ long pulses and cannot achieve broadband excitation, leaving severely distorted spectra for spin systems of large spectral range. Magic angle turning experiments [3–5] that employ only short pulses are promising for achieving excitation over a broad spectral range. Recently, we adapted Gan's MAT$^{\pm}$ experiment [6] to fast magic angle spinning with frequencies >20 kHz, hereafter referred to as fast MAT [7], to maximize the sensitivity by solving pulse timing issues due to finite pulses and short rotation periods. Fast MAT is presently the best broadband method to separate isotropic chemical shift and chemical shift anisotropy. It has been successfully applied to various tellurides with spectral ranges up to $\sim 1.8\gamma B_1$ without significant spectral distortions [7].

In this paper, we detail technical aspects of the fast MAT experiment, including analysis and quantitative numerical simulations of the nearly linear off-resonance phase shift, which can be considered as precession during the finite pulses and can therefore be included as an effective evolution time, and cyclic decrementation of the z-periods designed to keep them short in order to avoid T_1 relaxation or possible spin diffusion without the loss of required synchronization. For data processing, we have employed echo-matched full Gaussian time-domain filtering to improve the signal-to-noise ratio, taking advantage of moving echoes (when $t_2=t_1$) due to the refocusing of the isotropic chemical shifts. We have also applied the sharing-between-channels approach [8] after shearing to avoid spectral artifacts associated with digital rounding when shearing parameters are not integers.

In addition, PASS [2,9,10] and fast MAT are compared in terms of sensitivity, spectral distortions, and experimental implementation under similar conditions on a model sample. For relatively narrow spectra, PASS is preferable due to its better sensitivity, and simpler experimental set-up and data processing. However, for spectra whose width exceeds the pulse nutation frequency, the superiority of fast MAT in producing sideband-free spectra without significant spectral distortions is demonstrated.

2. Experimental

2.1. Samples

A mixture of seven amino acids with different ^{13}C labeling sites, including 1-^{13}C-Leu, 1-^{13}C-Gly, 2-^{13}C-Leu, 2-^{13}C-Gly, 3-^{13}C-Ala, 1-^{13}C-Ala, and 1-^{13}C-N$_\alpha$-(tert-butoxycarbonyl)-L-arginine, were

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used as a model sample. All of the labeled amino acids were purchased from CIL Inc. GeTe was used as received from GFS chemicals. Samples of $Ag_{0.53}Pb_{18}Sb_{1.2}Te_{20}$ and Sb_2Te_3 have been described in Ref. [11].

2.2. NMR parameters

All of the ^{125}Te NMR experiments were performed using a Bruker DSX400 spectrometer at 126 MHz for ^{125}Te. A 2.5-mm MAS probe head was used at a spinning speed of 21.74 kHz (synchronized with t_1 increments) with ^{125}Te 90° pulse length of 2.4 μs. All the fast MAT ^{125}Te spectra were obtained with the first five pulses of 2 μs and the last pulse of 3.5 μs in order to achieve broad excitation. EXORCYCLE phase cycling [12] was used for pulse length error compensation for the last pulse. Recycle delays of 150 ms for $Ag_{0.53}Pb_{18}Sb_{1.2}Te_{20}$, 50 ms for Sb_2Te_3, and 50 ms for GeTe were used. In the S^- MAT datasets, the number of t_1 increments was 400 for $Ag_{0.53}Pb_{18}Sb_{1.2}Te_{20}$, 280 for Sb_2Te_3, and 320 for GeTe, while in the S^+ MAT datasets, the number of t_1 increments was reduced to 80 for $Ag_{0.53}Pb_{18}Sb_{1.2}Te_{20}$, 40 for Sb_2Te_3, and 40 for GeTe. The ^{125}Te chemical shift relative to $Te(OH)_6$ in solution was calibrated using TeO_2 at +750 ppm as a secondary reference [13].

For all ^{13}C NMR experiments on the model compounds, a 4-mm double resonance MAS probe head was used at a spinning speed of ca. 3 kHz. Weak ^{13}C 22-μs 90° pulses were purposely applied to test off-resonance tolerance of fast MAT and PASS. Reference spectra using fast MAT and 5-pulse PASS were obtained with strong 4.4-μs 90° pulses.

3. Theoretical background and experimental setup

3.1. Gan's MAT experiment

Fig. 1 shows the basic pulse sequence used for MAT with a minimum number of pulses. Two evolution periods of duration $t_{1,nom}/2$ are each followed by a z-storage period that allows the rotor to reach a suitable orientation before evolution of transverse magnetization is resumed. Gan's modified MAT experiment, MAT$^{\pm}$ [6], achieves absorptive line shapes by using two slightly different versions of the pulse sequence. One of them is identical to the original MAT [3] with $t_{zA}=t_{zB}=t_r/3-t_1/2$, generating the MAT$^+$ dataset by combining signals for suitably chosen pulse phases [3]

$$S^+(t_1,t_2)=\left\langle \sum_{n=-\infty}^{\infty} S_n \exp\{i(\omega_{iso}-n\omega_r/2)t_1\}\exp\{i(\omega_{iso}+n\omega_r)t_2\}R \right\rangle, \tag{1a}$$

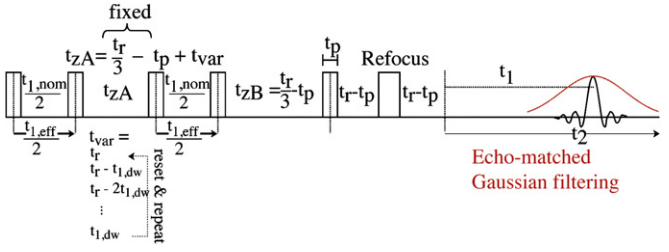

Fig. 1. Broadband fast MAT pulse sequence for obtaining pure isotropic-shift spectra and sideband separation. The unequal timings of the z-periods shown are for the "t_1 time-reversed" MAT$^-$ dataset, while the MAT$^+$ dataset is obtained with $t_{zB}=t_{zA}$, both decremented with increasing $t_{1,nom}/2$, illustrated by t_{var} values taken from the delay list, as shown at the bottom of the figure. Flip angles can be 60°–90° for the first five pulses of duration t_p, and 120°–180° for the last pulse. The pulse program is available from our website (http://www.public.iastate.edu/~nmrksr/). Echo-matched Gaussian filtering applied to the time domain signal to optimize the sensitivity is indicated schematically. For $t_{1,eff}/2=0$, a simplified pulse sequence with only the last two pulses is used (see text).

where t_r is the rotor period, S_n is the intensity of the nth order spinning sideband, and R accounts for relaxation effects. The other pulse sequence differs from the original one by an additional delay of $t_1/2$ before the last read-out 90° pulse, producing the "time-reversed" MAT$^-$ dataset

$$S^-(t_1,t_2)=\left\langle \sum_{n=-\infty}^{\infty} S_n \exp\{-i(\omega_{iso}-n\omega_r/2)t_1\}\exp\{i(\omega_{iso}+n\omega_r)t_2\}R \right\rangle. \tag{1b}$$

The sum and difference of these two datasets create cosine- and sine-modulated 2D datasets, respectively, which can be Fourier transformed to yield purely absorptive 2D spectra. After spectral shearing, 2D spectra with an "infinite-speed" isotropic-shift projection along ω_1 and anisotropic powder pattern or sidebands along ω_2 are produced.

Gan's original MAT experiments were performed at slow spinning speeds for narrow spectral ranges (<20 kHz), while for our purpose, spinning speeds greater than 20 kHz are necessary to maximize the sensitivity and cover the spectral ranges larger than 100 kHz needed due to wide chemical shift dispersion. Broadband spectra produce large phase shifts that can be explained as resulting from the evolution during pulses of finite duration. These lead to artifacts which can be corrected for as described below. Also, the rotor period t_r becomes short at fast spinning and the t_1 evolution time has to exceed one t_r to attain reasonable resolution, rather than $t_1<t_r$ at spinning speeds on the order of hundreds of hertz. Therefore, modifications of the durations of the z-periods (t_{zA} and t_{zB}) are necessary to maintain pulse synchronization as well as avoid T_1 relaxation and potential spin diffusion. Moreover, regular data processing procedures can be refined by employing echo-matched full Gaussian filtering to maximize the sensitivity and sharing between channels [8] after spectral shearing to eliminate spectral artifacts resulting from digital rounding with traditional shearing procedures.

3.2. Simulation of pulse excitation effects in fast MAT

In fast MAT experiments [7], four ~90° pulses are used in addition to the regular excitation and Hahn-echo pulse. Here, we analyze the effect of the pulses on magnetization off-resonance and show that the resulting phase shift, which is nearly linear with off-resonance frequency $\Delta\omega$, can be considered as precession during the pulses and thus compensated for.

The bandwidth of a single 90° x-pulse applied to z-magnetization is $2\gamma B_1$ if the full width at half maximum of the profile of the y-magnetization as a function of $\Delta\omega$ is considered [14]. However, the profile of the total transverse magnetization vs. $\Delta\omega$ is significantly wider, $>5\gamma B_1$ [15]. The difference arises from a nearly linear off-resonance phase shift $\sim\Delta\omega t_p/2$ [15] of the transverse magnetization.

The MAT sequence contains two pairs of ~90° pulses, with the first flipping z-magnetization to the transverse plane and the second restoring one magnetization component to z. It is instructive to start by considering one pair of ideal δ-pulses. The transverse magnetization generated by the first x-pulse precesses as

$$M_y=M_0\cos\Delta\omega t_1, \tag{2a}$$

$$M_x=M_0\sin\Delta\omega t_1. \tag{2b}$$

By the second pulse of suitable phase, either component can be stored along the z-direction

$$M_{z,\cos}=M_0\cos\Delta\omega t_1, \tag{2c}$$

$$M_{z,\sin}=M_0\sin\Delta\omega t_1. \tag{2d}$$