



Communication

Double-acquisition: Utilization of discarded coherences in a 2D separation experiment using the States method

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ABSTRACT

We propose a new data-acquisition scheme for 2D separation experiments to save the spectrometer time by 1/2. This scheme, referred to as a double-acquisition scheme, is applicable to most of separation experiments with the hypercomplex time-domain data-acquisition scheme (the States method) for data collection.

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In solid-state NMR, anisotropic interactions such as the dipolar interaction and the chemical shift interaction are often removed by dipolar decoupling and/or magic-angle spinning (MAS) to achieve high-resolution spectra. These anisotropic interactions, however, bear valuable information from which molecular structure and motional characteristics can be extracted, motivating us to develop techniques to recover the anisotropic interactions in one dimension and correlate them with the highly resolved signals in the other dimension. To name a few examples, Tycko et al. [1] showed that chemical shift anisotropies (CSA) can be observed under MAS by applying rotor-synchronized π pulses during the t_1 period, and Takegoshi and Terao [2] demonstrated measurement of ^1H -X dipolar interaction under MAS by FSLG-242.

In a 2D separation experiment, a pure 2D absorption spectrum in the indirect dimension (t_1) may be realized by the time-reversed precession method [3] that has been used for the 2D J -resolved experiment in solution NMR. In this method, two complementary experiments are done; one employs an 180° pulse inserted after the t_1 period while the other does not. Since an 180° pulse is prone to be marred by experimental imperfections as well as resonance offset, the time-reversed precession method is not suitable for the CSA/ ^1H -X dipolar separation experiments in solids. In fact, the above mentioned works applied an alternative approach using a 90° pulse for quadrature detection in the t_1 domain. In this approach, one applies a 90°_ϕ pulse after t_1 to convert the $I_{\phi+90^\circ}$ magnetization into the longitudinal one, while the I_ϕ magnetization is to be observed in the following detection period (t_2). The phase of

the 90° pulse is shifted by 90° to observe the $I_{\phi+90^\circ}$ magnetization in a complementary experiment with the same t_1 value (the States method) [4] or in a successive experiment with the next t_1 value (the TPPI method) [5]. Since the longitudinal magnetization is discarded in each experiment, the sensitivity is reduced by a factor $\sqrt{2}$ as compared to the time-reversed precession method [6].

In this work, we propose a new data-acquisition scheme in 2D separation experiments with the States method, in which the so far discarded longitudinal magnetization component is utilized. This scheme, referred to as a double-acquisition scheme, allows us to obtain a set of two complementary quadrature data in a single sequence, and thus hypercomplex data sets can be collected at double the speed compared with the conventional States method. From the sensitivity viewpoint, $\sqrt{2}$ -fold enhancement in signal-to-noise ratio would be expected for a given experimental time duration. We demonstrate the double-acquisition scheme for a 2D separation experiment of the ^1H - ^{15}N dipolar interaction using the FSLG-242 dipolar recoupling scheme under MAS, which eliminates the homonuclear dipolar interactions among the abundant ^1H spins while re-introducing the MAS-removed heteronuclear ^1H - ^{15}N dipolar interaction.

Fig. 1 shows a pulse sequence (a) and coherence transfer pathways for the first acquisition (b) and for the second acquisition (c) of the double-acquisition scheme designed for the FSLG-242 dipolar recoupling technique under MAS. After CP, the transverse ^{15}N magnetization evolves under the influence of the recoupled ^1H - ^{15}N dipolar interaction in the t_1 period. The second 90° pulse separates the ^{15}N magnetization into the transverse and longitudinal components, and the former is recorded as is done in the conventional experiment. When the longitudinal relaxation time T_1 is

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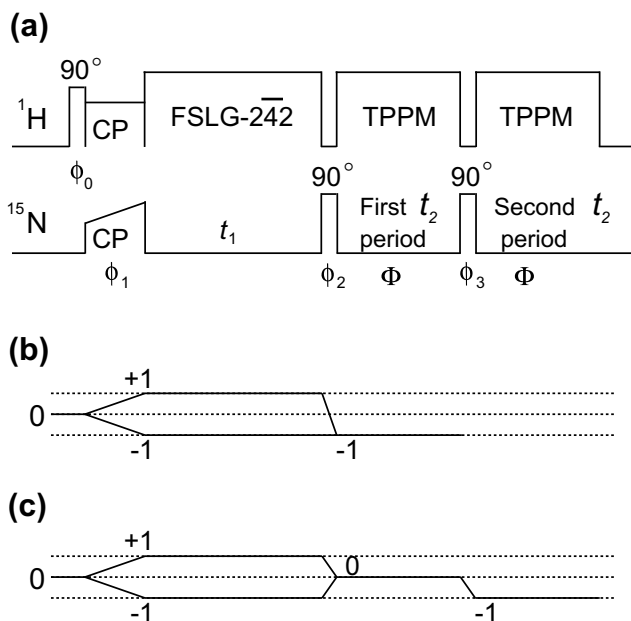


Fig. 1. A pulse sequence (a) and coherence transfer pathways for the first acquisition (b) and for the second acquisition (c) of the double-acquisition scheme designed for the FSLG-242 dipolar recoupling technique under MAS. ϕ_0 , ϕ_1 , ϕ_2 , ϕ_3 , and Φ denote the phases of the first ^1H excitation 90° pulse, the CP pulse, the 90° pulse after t_1 , the 90° pulse after the first t_2 , and the receiver phase, respectively. The phase cycles to obtain the t_1 -real data for the first acquisition and the t_1 -imaginary data for the second acquisition are: $\phi_0 = x, -x, \phi_1 = x, x, x, x, y, y, y, y, -x, -x, -x, -x, -y, -y, -y, -y, \phi_2 = x, x, -x, -x, y, y, -y, -y, \phi_3 = y, y, -y, -y, -x, -x, x, x, \Phi = x, -x, x, -x, y, -y, -y, -y, -x, x, -x, x, -y, y, -y, y$. The phase cycles to obtain the t_1 -imaginary data for the first acquisition and the t_1 -real data for the second acquisition are: $\phi_0 = x, -x, \phi_1 = -y, -y, -y, -y, x, x, x, x, y, y, y, y, -x, -x, -x, -x, \phi_2 = x, x, -x, -x, y, y, -y, -y, \phi_3 = -y, -y, y, y, x, x, -x, -x, \Phi = x, -x, x, -x, y, y, -y, -y, -x, x, -x, x, -y, y, -y, y$.

much longer than the transverse relaxation time T_2 , which is generally the case in solids, the latter longitudinal magnetization survives through the first t_2 period and can be used for the second acquisition. After the first t_2 period, another 90° pulse is applied to acquire the second FID during the second t_2 period. The FIDs collected in the first and second acquisitions are separately stored as a hypercomplex data set for a given t_1 by choosing a proper combination of the phases for the CP pulse and the second and third 90° pulses (ϕ_1, ϕ_2, ϕ_3). This procedure is performed for various t_1 increments to complete the 2D data. In the actual experiment, additional phase cycling was carried out to suppress artifacts and correspond to the limitation of our NMR system (Chemagnetics CMX Infinity-300) that allows only a single receiver phase (Φ) for the first and second acquisitions in the same scan.

To demonstrate the S/N gain with the double-acquisition scheme, we observed a ^1H - ^{15}N dipolar powder pattern under MAS in *N*-acetyl [1,2- ^{13}C , ^{15}N] DL-valine ([1,2- ^{13}C , ^{15}N] NAV), which was provided by Professor M. Kainosho at Tokyo Metropolitan University and his co-workers. The NMR experiments were carried out using a Chemagnetics CMX Infinity-300 spectrometer operating at a ^{15}N resonance frequency of 30.45 MHz with a doubly-tuned 5 mm CP/MAS probe (Doty Sci. Inc.). The rf-field intensity for both ^1H excitation 90° pulse and CP was 62.5 kHz, and both the nutation and the phase-modulation angles in the TPPM decoupling [7] were optimized for an rf intensity of ≈ 80 kHz to be 180° and $\pm 7.5^\circ$, respectively. The contact time for CP was 4.5 ms. The MAS frequency ν_{MAS} was 10 kHz and found to be stable within 0.1% without active air regulation. To suppress the spin echo in the second t_2 period, we inserted a z-filter during which ^1H irradiation is suspended between the first t_2 period and the

third 90° pulse (not shown in Fig. 1 for clarity). The duration of the z-filter was 25.6 μs .

For the 2D FSLG-242 sequence, the rf-field intensity and the corresponding switching frequency were 71.0 kHz and 50.2 kHz, and the corresponding duration time for a 2π LG pulse was 11.5 μs . The intervals for phase and frequency jump were 0.2 and 0.8 μs . These settings are to fulfill the $n = 1$ recoupling condition for the FSLG-242 sequence for the MAS frequency at 10 kHz. For the first and second acquisition, 1024 data points were collected with a sampling interval of 51.2 μs . Sixteen FIDs were accumulated for each t_1 value with a relaxation delay of 2.0 s, and spectra were recorded for 64 values of t_1 with an increment of 50.0 μs . The experiment was carried out at room temperature, and the total experimental time was about 72.9 min. Before two-dimensional Fourier transformation, the FIDs were zero filled in the t_1 dimension to 256 data points.

Fig. 2 shows 2D FSLG-242 spectra of [1,2- ^{13}C , ^{15}N] NAV obtained by the double-acquisition scheme (a) and the conven-

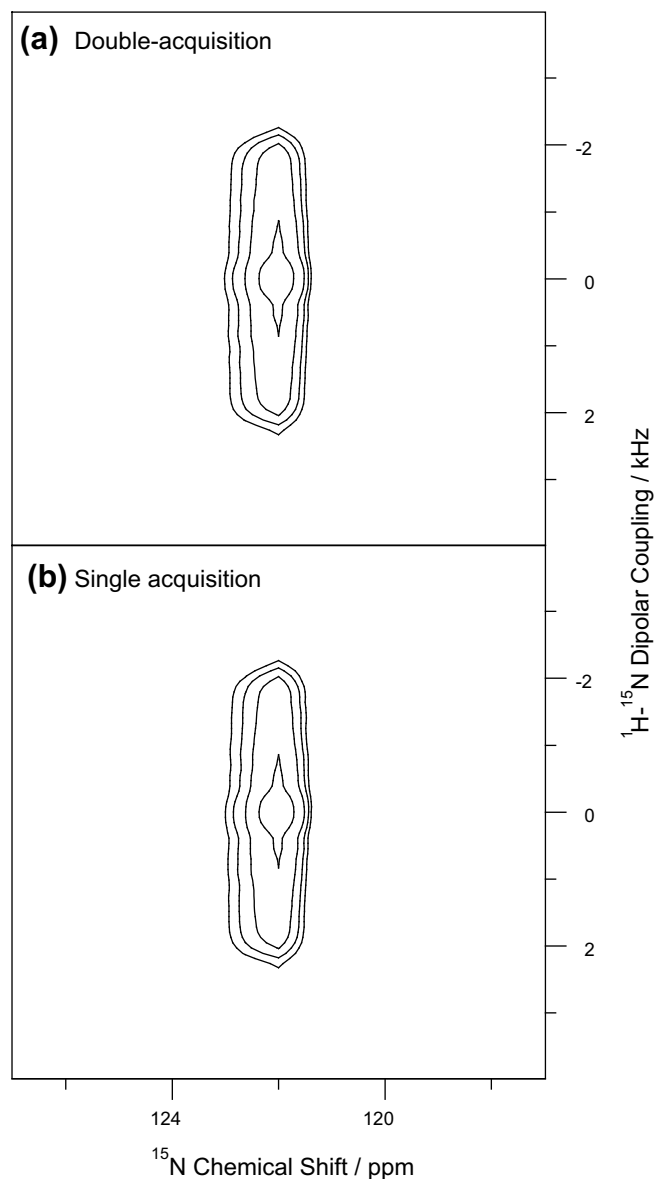


Fig. 2. 2D FSLG-242 spectra of [1,2- ^{13}C , ^{15}N] NAV obtained by the double-acquisition scheme (a) and the conventional single acquisition scheme (b). The experimental times were 72.9 min for (a) and 70.2 min for (b).

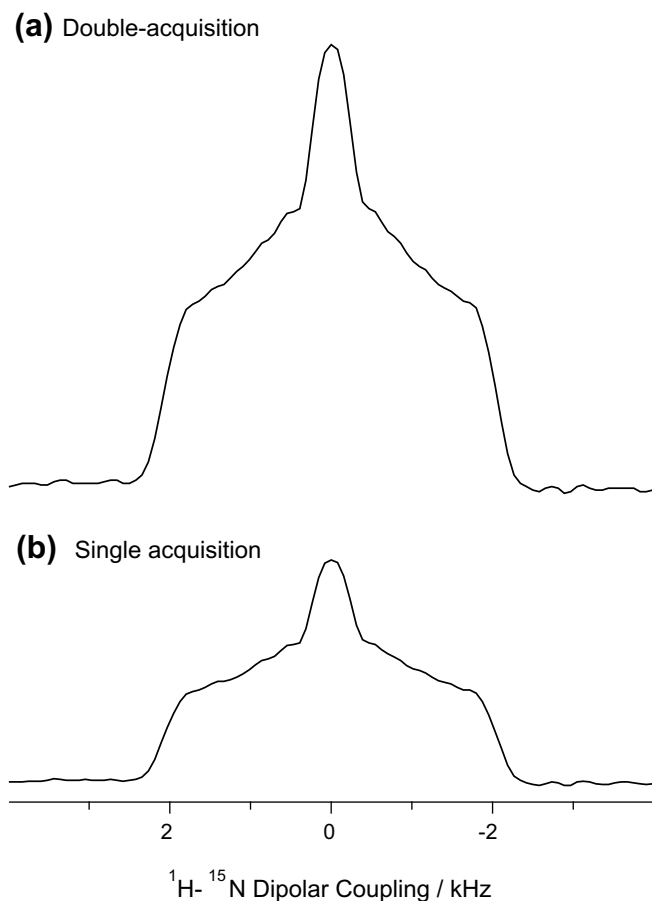


Fig. 3. The f_1 slice spectra of the 2D FSLG-242 spectra of $[1,2\text{-}^{13}\text{C}, \text{}^{15}\text{N}]$ NAV acquired by the double-acquisition scheme (a) and the conventional single acquisition scheme (b). The spectra are plotted with the same vertical scale for comparison.

tional single acquisition scheme (b), and their respective slice spectra along the f_1 dimension are depicted in Fig. 3 (a) and (b). No intentional vertical scaling was performed in Fig. 3. Note that ca. $\sqrt{2}$ -fold enhancement in signal-to-noise ratio was attained in (a) as compared to that in (b) within nearly identical experimental times of 72.9 min for (a) and 70.2 min for (b), while no appreciable spectral distortion was found. The present double-acquisition scheme can also be used with the TPPI method, although its incorporation is not very straightforward and outside the scope of this paper.

To summarize, we have proposed the double-acquisition scheme for a 2D separation experiment, in which a pure absorption 2D spectrum equivalent to that in the conventional single acquisition scheme can be obtained in half the acquisition time. Alternatively, this scheme doubles the number of signal accumulations in a given experimental time. This work corresponds to one possible application of the idea of acquiring two separate data during a single sequence, firstly demonstrated in the COmbined COrelated and Nuclear Overhauser enhanced Spectroscopy (COCONOSY) [8] and the COSY-NOESY [9] experiments, and later in the COmbined COrelated and Dipolar-Assisted Rotational Resonance (COCODARR) technique [10]. These previous works are categorized into the scheme for simultaneous data acquisitions for a pair of distinct sequences, while the present approach of the double-acquisition aims at efficiently collecting the data sets for a single 2D spectrum.

For ^{13}C detected experiments in uniformly ^{13}C labeled systems, double-acquisition can cause additional cross peaks arising from the ^{13}C spin-diffusion. Nevertheless, such cross peaks appearing in the f_1 dimension can readily be identified and disturbance is expected to be small.

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