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Ultrafast acquisition of ^1H - ^1H dipolar correlation experiments in spinning elastomers

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Abstract

We show that two widely used 2D solid-state NMR (ssNMR) pulse sequences can be implemented in an ultrafast (UF) manner, and yield 2D spectra of elastomers in a single scan, under magic-angle spinning. UF 2D ssNMR provides an acceleration of one to several orders of magnitude for classic experiments.

Keywords: ultrafast NMR, solid-state NMR, double quantum, spin diffusion

Introduction

Multidimensional nuclear magnetic resonance spectroscopy (NMR)[1,2] is a major tool for elucidating the structure of solid samples in chemical, materials and biological sciences.[3–6] Classic 2D NMR spectroscopy, however, relies on a scheme that is intrinsically time-consuming, even when ample sensitivity is available. This is due to the need to repeat multiple 1D sub-experiments to sample incrementally the additional time dimension. This long experiment duration is a major obstacle to the analysis of samples with very long longitudinal relaxation times, which include a variety of organic and inorganic materials. It also prevents the acquisition of detailed structural information, which is usually obtained in the form of series of 2D experiments.[7,8]

Several strategies have been developed to overcome the speed limitations of multidimensional (ND) solid-state NMR (ssNMR). Paramagnetic doping is a convenient method to shorten relaxation delays, with the caveat of possibly inducing unwanted structural changes.[9] More recently, “non-uniform sampling” (NUS) schemes have been implemented, which consist of collecting only a randomly selected subset of increments, and using non-Fourier processing methods.[10,11] In solution-state NMR, the most dramatic acceleration of ND acquisitions is obtained with the so-called “ultrafast (UF) NMR” approach, which makes it possible to acquire 2D NMR spectra within a single scan.[12] UF NMR relies on a spatial rather than temporal encoding of the NMR interactions. Resonances are encoded with a combination of bipolar gradients and linearly frequency-swept pulses, and decoded during acquisition with an echo-planar spectroscopic imaging (EPSI) scheme. Applications of liquid-state UF NMR have been reported in a variety of fields such as metabolomics, real-time reaction monitoring, or hyphenated techniques such as chromatography or dissolution dynamic nuclear polarization (DNP).[13] The possibility to accelerate ND ssNMR experiments with spatial encoding, however, remains largely unexplored.

Magic-angle spinning (MAS) probes are rarely equipped with a magnetic field gradient. While “high-resolution MAS” (HR-MAS) probes more commonly have gradients, and may be used for UF 2D NMR,[14] they do not deliver the radio-frequency (RF) power needed for most ssNMR experiments. Gradient-enhanced experiments may still be carried out, using a standard ssNMR probe together with external microimaging gradients.[15,16] In a pioneering study, Frydman and co-workers used such a setup to acquire UF NOESY spectra of rubber samples. They also characterised the detrimental effects of misalignments of the rotor spinning axis and the magnetic field gradient.[17] An alternative was also proposed, based on orientational encoding.[18] Nonetheless, to the best of our knowledge, no UF implementation of an ssNMR pulse sequence has been reported.

In this communication, we show that two of the most widely used 2D ssNMR experiments, double-quantum correlation (DQ)[19,20] and RF-driven proton spin diffusion (PSD)[21,22] can be recorded in a single scan, using spatial encoding. We chose to investigate ^1H correlation experiments since they offer optimum sensitivity and spectral width conditions for UF experiments. These experiments are performed at very high field (17.6 T), using a double resonance MAS probe together with microimaging gradients, on a natural rubber sample. Such ultrafast 2D experiments make it possible to expedite the acquisition of spin-diffusion build-up curves, which are a central tool for structural studies in disordered solids.

Results and discussion

The pulse sequences for ultrafast double-quantum correlation experiments (UF-DQ) and proton spin diffusion (UF-PSD) are shown in Fig. 1. Their main features compared to their conventional counterpart are i) the replacement of the conventional t_1 incremented evolution by a spatial encoding block consisting of a pair of 180° chirp pulses applied during alternating gradients; ii) the replacement of the conventional detection by an EPSI scheme. Pulsed field

gradients are used also for coherence selection, a feature that is rarely used in solid-state NMR and that is found to work appropriately here. The other pulse sequence elements are similar to those of conventional pulse sequences. In the UF-DQ experiment, rotor-synchronized back-to-back (BABA) 90° radiofrequency pulse cycles[23] are applied during 3.28 ms (64 rotor periods) to generate double quantum coherences between dipolar-coupled spins. During the reconversion period, BABA cycles are used again to reconvert double quantum coherences back to longitudinal magnetisation. In the UF-PSD experiment, radio frequency-driven recoupling (RFDR) 180° radiofrequency pulse cycles with xy-8 phase alternation are used to reintroduce dipole-dipole couplings during the mixing period and induce a transfer of longitudinal magnetisation.[21]

Two complementary measures were taken to avoid interferences between sample rotation and the periodic acquisition gradient train.[14] First, a composition of the gradients along the three physical axes was used to yield a spatial encoding gradient sufficiently aligned with the MAS axis. This alignment is obtained by careful calibration on a silicone sample (see SI). Second, the duration of a readout gradient (T_a) is chosen to be an even multiple of the rotor period. With these precautions, echo trains of 131 ms were recorded without significant signal losses due to interferences, and no spinning sidebands were observed.

The UF-DQ and UF-PSD spectra of a sample of natural rubber are shown in Fig. 2, together with their conventional counterparts. The UF-PSD spectrum was recorded in a single scan of 275 ms, which is over 500 times faster than the conventional spectrum. For the UF-DQ spectrum, 8 scans were accumulated, in order to observe the least intense cross peak. While not single-scan, the UF experiment remains much shorter than the conventional one.

A comparison between UF and conventional spectra reveals that the UF implementation yields the same information, in a much shorter time. Note that the conventional spectra were also acquired using pulsed-field gradients for coherence selection and no phase cycling. The

UF spectra were recorded with folding in the direct dimension to optimize the compromise between spectral widths, resolution and gradient amplitudes –a well-known feature of UF experiments.[13] The appropriate spectral width to avoid overlap can be determined from the 1D spectrum. If needed, a larger spectral width could be recovered by means of interleaving, albeit at the cost of an extended experiment time.[24,25] One should also note that the resolution of UF spectra is governed by intrinsic characteristics of UF pulse sequences, as already described for liquids.[26–29] In particular, a compromise has to be set along the indirect dimension between resolution, spectral width and sensitivity. The UF spectra also display a peak splitting at 2.98 ppm in the conventional dimension, along with an important sensitivity loss, which is not observed in the conventional ones. The sensitivity loss is due to a short- T_2 component, as illustrated in Fig. 2. The supplementary modulation observed, leading to the splitting of the peak, has not been analyzed in detail, but it illustrates the limitation of the method for samples with short T_2 values. It should also be noted that, in the conventional DQ experiment, the cross-correlation peaks show elongated lineshapes (along the DQ diagonal with a slope of 2) characteristic of correlated disorder.[30] These features are however masked in the UF-DQ spectra due to apodization in the ultrafast dimension.

Accelerated acquisitions are particularly promising for arrayed 2D experiments, e.g., for the acquisition of DQ or PSD build-up curves. Such data plays a central role in the structural characterization of solids by NMR, but the corresponding experiments are time-consuming due to the need to acquire multiple 2D spectra. Figure 3 shows experimental spin diffusion build-up curves, obtained on a natural rubber sample with a series of UF experiments compared to conventional experiments. The UF implementation is considerably faster than the conventional one, since only 5 min are necessary to record the UF spin-diffusion curves, versus 57 min with the conventional pulse sequence. A qualitative agreement is observed between UF and conventional curves. Several key features, such as the initial delay of some build-up curves

(e.g., $\text{CH} \rightarrow \text{CH}_3$) or the bell shape of the $\text{CH}_2 \rightarrow \text{CH}$ curves, are well captured by the UF implementation. The offset observed in some cases between UF and conventional build-up curves, as well as the non-zero initial values for some cross-peaks, are due to peak overlap and residual artefacts (see the caption of figure 3). Future developments will consider improving the spectral resolution of UF spectra through alternative spatial encoding schemes. Such offsets could also be accounted for at a modeling stage. The quantitative description of spin diffusion in such complex sample, however, is beyond the scope of this communication.

This type of curves can provide relevant qualitative information about complex samples. By offering the possibility to acquire the entire data set more than 10 times faster than its conventional counterpart, the UF-PSD MAS pulse sequence appears as a promising tool to perform a quick and advanced screening of real systems of industrial interest such as complex polymers.

While it may provide a dramatic acceleration for a variety of samples and experiments, UF MAS NMR will be of limited use when dealing with short transverse relaxation times, since the spatial encoding duration cannot be reduced significantly without resolution losses.[26] Thus, the ultrafast method will prove to be particularly useful in the case of soft, compared to hard solids characterised by short transverse relaxation times. Nevertheless, the study of a broad variety of materials could benefit from the acceleration offered by this technique. In addition, UF 2D NMR suffers from well-characterised sensitivity losses due to the single-scan nature of the experiment, or to the large frequency dispersion induced by the gradients during acquisition, as well as from artefacts arising in MAS-UF NMR potentially masking the low intensity cross peaks.[14] These specific features of UF experiments have been widely characterized in previous studies, whose conclusions also apply to the present methods.[13]

Improvements may be obtained, at a reasonable time cost, with the use of “hybrid” multi-scan methods.[31]

Conclusion

We have shown that two of the most widely used solid-state NMR experiments can be recorded in a single scan, using spatial encoding. Such ultrafast experiments are particularly promising for structural studies by solid-state NMR, which require arrays of 2D spectra. UF 2D ssNMR experiments will also prove useful for applications to samples with long longitudinal relaxation times. The sensitivity requirements of UF 2D NMR can be commonly met for nuclear such as ^1H or ^{31}P and may be extended to other nuclei with dynamic nuclear polarisation. The ultrafast method could also be used to speed up higher dimensional solid-state experiments in a pure ultrafast fashion [32] or in an hybrid fashion [33], leading to an acquisition time for a 3D experiment equivalent to a conventional 2D experiment.

Experimental

All the measurements were carried out on a Bruker AVANCE III spectrometer operating at a magnetic field of 17.6 T (corresponding to ^1H Larmor frequency of 750.13 MHz), equipped with a Bruker 3.2 double resonance MAS probe and a Bruker Micro 2.5 gradient system (triple axis, 2.5 G/cm/A, 40 A/axis).

To apply a gradient exactly along the MAS axis, the three laboratory-frame gradient coils have to deliver the same gradient strengths. The currents applied to the three coils were thus carefully adjusted by maximizing the center band intensity in a 1D profile of a rotating cylindrical silicone sample when applying combinations of two (of the three) laboratory-frame gradients. The intensity maximum is obtained when the resulting gradient is perpendicular to the MAS axis (corresponding to equivalent intensities of the two applied gradients). The spinning frequency was set to 19532 Hz, such that the duration of an acquisition gradient (1024 μs) was an even multiple of the rotor period (51.2 μs).

For all the ultrafast (UF) experiments, spatial encoding was performed by using a constant-time scheme, consisting of a double spin echo with 8 ms smoothed chirp encoding pulses. The sweep range of the encoding pulses was set to 20 kHz. The amplitude of the encoding gradients was adapted to obtain a frequency dispersion equivalent to the frequency range of the pulses: 0.052 T/m. The acquisition block used 64 detection gradient pairs. The duration of each acquisition gradient was 1024 μ s with an amplitude of 0.433 T/m. A single scan was recorded for the UF-PSD spectrum; 8 scans were recorded for the UF-DQ spectrum, with a recovery delay of 3 s. Coherence selection was performed by 1024 μ s gradients as indicated in Figure 1a with 0.727 T/m and 0.346 T/m gradient amplitudes for the UF-DQ experiment, and as indicated Figure 1b with 1.039 T/m and 1.143 T/m gradient amplitudes for the UF-PSD experiment. The specific processing of the UF spectra was performed with a home-written Matlab routine. A sinusoidal apodization was applied in the direct dimension and a spatial Gaussian apodization was applied in the indirect dimension.[34] Zero-filling was applied in both dimensions as described in reference 29 for the indirect dimension.

The conventional DQ spectrum (Fig. 2a) was acquired with 16 dummy scans, 256 t1 increments and 4 scans with a recovery delay of 0.25 s, resulting in an acquisition time of approximately 5 min. The conventional PSD spectrum (Fig. 2c) was acquired with 8 dummy scans, 256 t1 increments and 8 scans with a recovery delay of 0.25 s, resulting in an acquisition time of approximately 9 min. Phase cycling was performed in 8 steps for the DQ experiment, and 4 steps for the PSD experiment. For these two spectra, an exponential apodization was performed in both dimensions, and zero-filling was only used in the direct dimension.

For PSD build-up curves (Fig. 3), 26 conventional PSD and UF-PSD spectra were acquired. The conventional ones were acquired with 8 dummy scans, 128 t1 increments and 4 scans with a recovery delay of 0.25 s, resulting in an acquisition time of 130 s. Phase cycling was performed in 4 steps. A sinusoidal apodization and zero filling were applied in both

dimensions. UF-PSD spectra were acquired and processed with the same conditions as those described for figure 2d. Peak volumes were determined with Topspin 3.2, and the whole datasets were normalized with Matlab in order to minimize the global intensity differences between UF and conventional curves.

In the UF-DQ experiment, rotor-synchronized back-to-back (BABA) 90° radiofrequency pulse cycles [23] were applied during 3.28 ms (64 rotor periods) with a radio frequency field of 80 kHz to generate double quantum coherences between dipolar-coupled spins. The same number of BABA cycles was used to reconvert double quantum coherences back to longitudinal magnetisation. In the UF-PSD experiment, radio frequency-driven recoupling (RFDR) cycles with xy-8 phase alternation were employed to promote longitudinal magnetisation transfer during the mixing period.[21]

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Figures

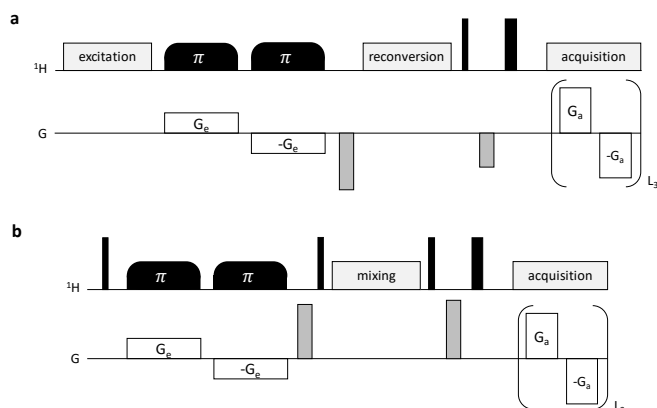


Fig. 1 (a) UF-DQ and (b) UF-PSD pulse sequences. Narrow and wide black vertical bars represent 90° and 180° hard pulses, respectively. Gradients for coherence selection are shown in grey. G_e is the spatial encoding gradient and G_a the acquisition gradient.

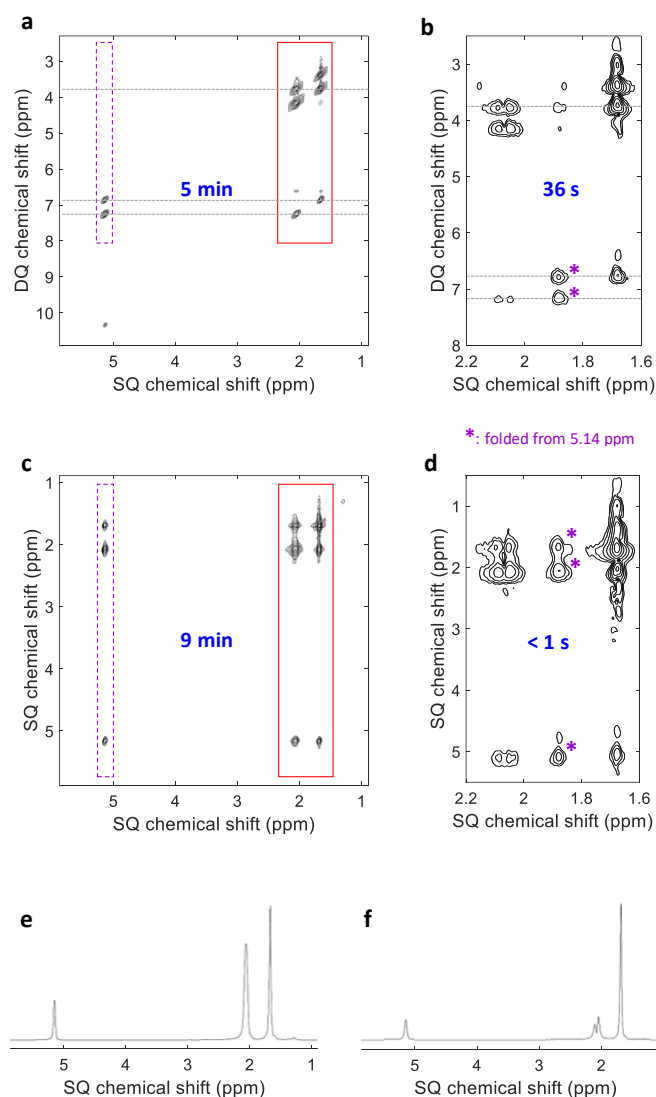


Fig. 2 Conventional (a) and ultrafast (b) DQ spectra spectra of a natural rubber sample recorded in 5 min and 36 s, respectively. Conventional (c) and ultrafast (d) PSD spectra of the same sample, recorded in 9 min and less than 1 s, respectively. The spectral regions displayed in the ultrafast spectra are highlighted by a red square in the corresponding conventional spectrum, while the folded region appears in purple. 1D spectra of this sample, with a non-delayed (e) and a delayed (f) acquisition, show the peak shape deformation of the peak at 2.08 ppm.

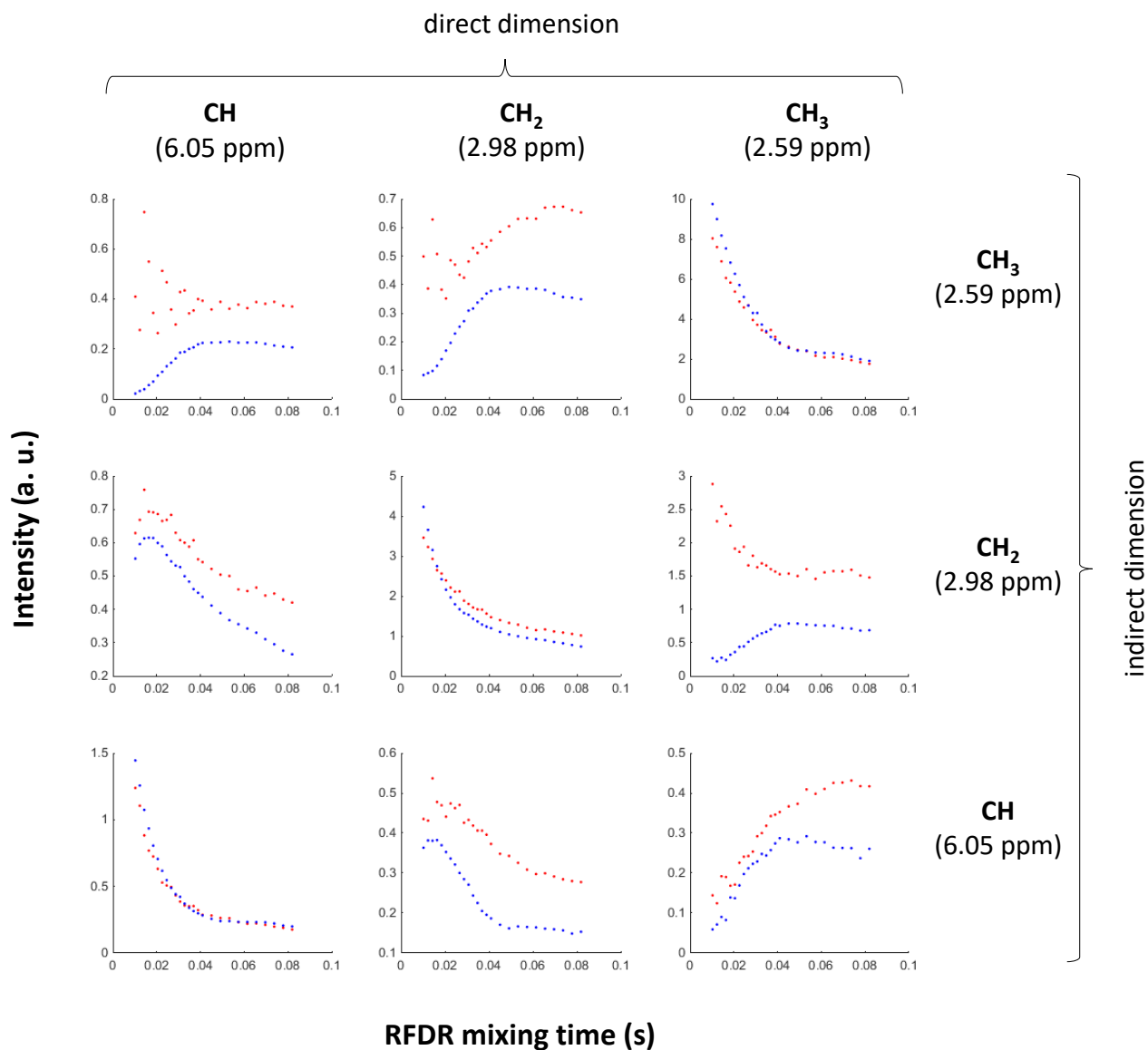


Fig. 3 2D peak volumes (ssUF-PSD in blue and conventional ss-PSD in red) as a function of the spin diffusion mixing time for the 9 peaks observed in the 2D spectrum. The discrepancy observed at short mixing times between conventional and UF curves for the $\text{CH}_2 \rightarrow \text{CH}_3$ cross-peak is due to a peak overlap in the UF indirect dimension (middle-right graph). As well, the dispersions of UF cross-peak intensities at short mixing times for the $\text{CH}_3 \rightarrow \text{CH}_2$ and $\text{CH}_3 \rightarrow \text{CH}$ cross-peaks is partly related to peak overlap and to the presence of weak intensities artefacts (top-left and -middle graphs).