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Bandwidth Extension in Noise Spectroscopy

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Noise spectroscopy has previously been demonstrated to provide broad-bandwidth excitation with minimal applied RF field strengths. Nonetheless, its application to broadline solid-state NMR spectroscopy has appeared limited by the need to have unrealistically short probe- and receiver-recovery times after pulses. In this Communication, we explain theoretically and demonstrate experimentally that accurate lineshapes can be observed in ^{2}H solid-state NMR spectroscopy even where the probe ringdown time greatly exceeds the required time between sampled data points. Moreover, accurate lineshapes can be observed to ±125 kHz using RF fields as weak as a few hundred hertz.

Key Words: **noise; wideline NMR; ^{2}H powder patterns.**

INTRODUCTION

One tempting feature of noise spectroscopy and its application in solid-state nuclear magnetic resonance is the claim that the traditional link between the strength of the excitation field, ω_1, and the undistorted spectral bandwidth, $\Delta\omega$, is effectively broken, and that wideline *absorption* spectra of (at least in principle) unlimited bandwidth might be observed. As described by Ernst and by Kaiser (*1, 2*), broad excitation bandwidths are achieved by appropriate randomization of the phases and/or amplitudes of the irradiation field, while the rate at which the magnetization is sampled—once in the time between pulse, Δt—determines the spectral bandwidth (*3*). By minimization of Δt it would therefore appear possible to theoretically increase the bandwidth without limitation.

In practice, however, a different experimental problem familiar from high-power NMR experiments generally limits the bandwidth achievable in conventionally executed noise spectra. Tuned circuits, as are found in traditional probes, and high-performance receivers designed to sense signals many orders of magnitude smaller than the applied RF fields cannot faithfully reproduce those signals instantaneously after the pulsed RF fields are turned off, and recovery times increase with increasing pulse power. Broad bandwidth spectra as are found in ^{2}H spectroscopy may require >60 dBm (1 kw) of RF power to excite and typically cannot be observed until at least 10–15 μs after the pulse is turned off. To recover information lost in this initial evolution period, spin-echo methods are generally preferred—though the distortions thereby generated can be considerable, in particular where the spin-echo timescale is comparable to internal dynamical timescales. Even in noise spectroscopy, where the excitation is effected by comparatively gentle pulses (typically 0–10 dBm), receiver dead times much less than 5 μs are difficult to achieve—particularly at low resonance frequencies. Thus while noise spectra of dynamically averaged deuterium quadrupolar powder patterns have appeared (*3, 4*), the broadband spectrum of a ^{2}H nuclear spin in a static C-H bond—where the Pake pattern may extend over ~250 kHz—has not previously proven amenable to noise excitation methods.

In this Communication we explain how it is possible to observe powder patterns of arbitrary width, without extensive modification of either existing probes or receivers, using noise excitation in NMR. The key to our method of bandwidth extension in noise spectroscopy is the realization that there is no requirement derived from the theoretical derivation for the traditional synchronization of pulse repetition rates (Δt) and data acquisition rates (τ_{samp}). In point of fact, the fundamental limitation on bandwidth in noise excitation experiments operating in the linear response limit is, instead, simply the length of the excitation pulse (τ_p), largely independent of the rate of application to the spin system.

We proceed in this Communication by reviewing the noise experiment with an eye towards generating a better understanding of the features which contribute to limiting the bandwidth. Of course, more systematic introductions are available elsewhere (*3, 5–9*). First, we discuss the problem of excitation; thereafter, we proceed to a discussion of the evolution of the magnetization in between pulses. Finally, we address the issue of data accumulation in a form appropriate for further conventional analysis.

DISCUSSION

1. Excitation Sequences

The assumption which drives noise experiments of the sort described in this work is that the system response is linear in the experimental input—i.e., that the irradiation sequence, however it may appear, is sufficiently weak so that each spin packet responds only to the effective RF field on-resonance for that packet.

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Typically, the experimental goal is uniform excitation over a broad bandwidth. The amplitude of a signal detected in a noise experiment is then proportional to the amplitude of the field component at that frequency—of course, subject to the limitation that the system always responds linearly with respect to the input field.

Unlike the analogous situation in FTIR, in NMR the irradiation fields are typically coherent. Furthermore, it is impractical to sample the evolving signal in the presence of the applied field. As a result, any noise-based experiment must consist of pulses manipulated so as to destroy the natural coherence of the irradiation field, and separated by windows adequate to sample the excited and evolving magnetization. For most one-dimensional spectroscopic applications, a family of broadband sequences known as maximal length binary sequences (MLBS's) are particularly robust (*10–12*). Such pulse trains involve only pseudorandom 0–180° phase shifts and can be generated from tabulated shift-register based algorithms. The envelope of the power spectrum of an MLBS sequence of pulses of length τ_p is identical to that of a single pulse of similar length, and so the effective field falls off as $\sin(0.5\omega\tau_p)/0.5\omega\tau_p$. For pulses of length $\tau_p = 300$ ns, this implies a bandwidth (defined as the maximum frequency at which the field intensity profile is 98% as strong as that found near resonance) of ± 260 kHz, which should be more than adequate for ^{2}H NMR spectroscopy—as long as the probe circuitry is similarly broad band.

2. Magnetization Evolution

Once excited, magnetization evolves at its natural frequency. As in traditional NMR, the Nyquist frequency ω_N is precisely $\frac{1}{2}\tau_{\text{samp}}$, the time interval between sampled data points. Traditionally, $\tau_{\text{samp}} = \Delta t = \frac{1}{2}\omega_N$, and probe recovery times as long as 5 μs would appear to limit the available total bandwidth to approximately ± 100 kHz.

3. Processing Considerations

The confusing aspect of noise spectroscopy is that the raw data bears little resemblance to a traditional free induction decay. Each new pulse in the sequence generates transverse magnetization which evolves superposed atop all previous and future excitations. Thus there is no apparent decay to the signal output in a noise-excited spectrum—and often, little can be obviously associated with signal.

Where the excitation consists of a sequence of J small-amplitude pulses repeated cyclically, the traditional signal function $\mathcal{S}(j)$ can, however, be extracted from the (discretely represented) pulse sequence $P(l)$ and the sampled magnetization function $M(l)$ via

$$\mathcal{S}(j) = \sum_{i=0,J-1} P(i)\,M(i+j), \qquad [1]$$

where the second index $i + j$ is cyclic with period of J. In a well-designed experiment, $\mathcal{S}(j)$ will be dominated by noise for some value of $j < J$ and the cross-correlation procedure can be truncated at that point. The cross-correlation reshuffles and phases each of the individual free induction decays, yielding a macroscopic response function of amplitude comparable to that observed by strong-pulse methods in similar amounts of averaging time.

4. Extending the Bandwidth

Our procedure for extending the bandwidth is quite simple indeed. While the MLBS sequence corresponds to a sequence of pulses of relative amplitudes 1 and -1, we can fill in the sequence with fictive "pulses" of amplitude 0 without affecting the excitation properties of the MLBS. Instead of attempting to overcome the inevitable limitations imposed by the required recovery time after pulses, we instead maintain pulses on a timescale Δt long compared to the recovery time of our system, and sample the evolving signal function at time points spaced by τ_{samp}—as if each such point followed a pulse of 0 amplitude at the same, shorter time scale. Subsequent explanations are simplified if we assume that $\Delta t = n\tau_{\text{samp}}$ for n some integer, though this is not a requirement of the method. Under these conditions, $M(l)$ is nJ points long, and ω_N is extended n-fold. Simultaneously, the pulse input record $P(l)$ is redefined to account for the additional $(n-1)J$, zero-amplitude points, as if it too were sampled in increments of τ_{samp}. Summing over all points $\{0, \ldots, nJ-1\}$, the signal function $\mathcal{S}(t)$ is calculated as in Eq. [1].

Due, however, to the inevitable overlap of pulses with some of the sampled output points, the signal record $M(l)$ contains numerous periodically recurring errors. We therefore define a series of p experiments leading to signal functions $\{S_1, S_2, \ldots, S_p\}$. In each experiment, we maintain the same τ_{samp}, but vary $n = \{n_1, n_2, \ldots, n_p\}$ so that the pulse spacings Δt_n differ systematically.

Each signal record $M_n(l)$ is flawed by the periodic reappearance every Δt_n of points which, ideally, would be sampled during a subsequent pulse leading inevitably to distortions in $\mathcal{S}_n(l)$. Nonetheless, it is a simple matter to choose $\{n_1, n_2, \ldots, n_p\}$ so that each subsequent experiment fills in some of the time points missing from all prior data records. In this fashion, and as is illustrated in Fig. 1, all points required to complete $\mathcal{S}(j)$ to arbitrary J can be sampled.

5. Filling in the Blanks

Given p data records representing experiments acquired with $\Delta t/\tau_{\text{samp}} = n_1, n_2, \ldots, n_p$ we are confronted with the question of how to combine data sets so as to provide a single faithful representation of the signal record, $\mathcal{S}$. In principle, any point in j in $\mathcal{S}(j)$ is calculated by a weighted average over each data set

$$\mathcal{S}(j) = \sum_n a_{n,j}\mathcal{S}_n(j), \qquad [2]$$

where the $a_{n,j}$ are the weighting factors appropriate to the jth

point in the nth record. Finding the correct $a_{n,j}$'s is simplified considerably by two features of the experiment:

(1) We have previously provided an analytic expression which predicts the noise signal intensity as a function of all relevant experimental parameters (the flip angle per pulse $\alpha = \omega_1\tau_p$, the pulse spacing Δt, and the system T_1 (*9*). For excitation using an MLBS, where α is small the variation in intensity with Δt is negligible.

(2) For τ_{samp} fixed across all data sets, many of the actual sampled data points will represent the same time point in the overall sequence. These common data points can be used to further evaluate the need for amplitude corrections.

Under these conditions a gap-free data set can be calculated by weighting each appearance of a given time-point by $\frac{1}{q}$, where q is the number of data sets in which it appears far removed from a pulse.

The short-time points in $\mathcal{S}$, however, provide a different challenge. In no data set can we observe the actual signal which should have been acquired during the ringdown period. Thus, substantial effort must be made to minimize the dead time, from whatever source. We discuss how we deal with the absence of a small number of early-time points below.

EXPERIMENTAL

In Fig. 1, we demonstrate the procedure used to acquire the data set whose Fourier transform is shown in Fig. 2, where we present the 200-K ^{2}H NMR spectrum of perdeuterated poly(ethylene oxide), d-PEO. The applied RF power was ~13 dBm and $\tau_p \approx 300$ ns, though the length of a pulse is poorly defined due to the finite turn-on times of the spectrometer gates and of the pulse in the probe. For comparison, in this probe and operating under more typical conditions for ^{2}H NMR (applied pulse power 61 dBm) the 90° pulse is ≈2.2 μs), so $\alpha < 0.1°$. Data sets are acquired with $\tau_{\text{samp}} = 1.8$ μs and $\{n_i\} = \{7, 9, 11, 13\}$. Careful adjustment of the probe, including some modest Q-damping, and of the receiver protection circuitry reduced the recovery time of the spectrometer to <3.0 μs.

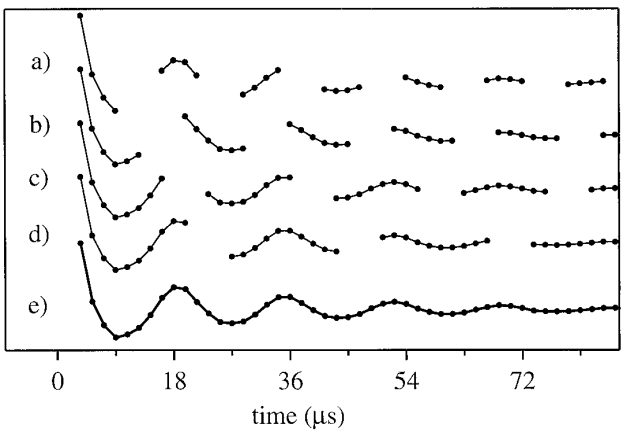

FIG. 1. Signal decay functions, after cross-correlation, for a series of noise excitation sequences (a) $\Delta t = 12.6$ μs; (b) $\Delta t = 16.2$ μs; (c) $\Delta t = 19.8$ μs; (d) $\Delta t = 23.4$ μs; applied at the ^{2}H resonance frequency of perdeuterated poly(ethylene oxide) (d-PEO). The sample was cooled to 200 K, and an MLBS sequence containing 511 pulses was applied with $\tau_{\text{samp}} = 1.8$ μs. In each sequence, the first two desired sampling points are missing; thereafter, periodic gaps of 3 points long appear in the data record. (e) The gapless free induction decay, sampled at $\tau_{\text{samp}} = 1.8$ μs, made by combining data points from each of the previous data records.

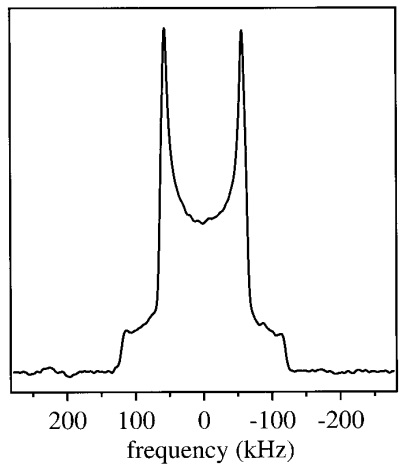

FIG. 2. Fourier transform ^{2}H absorption NMR spectrum of d-PEO at 200 K, derived from the set of noise-excitation experiments as described in Fig. 1. The free-induction decay was back-extended to zero time using linear prediction, zero-filled to 4096 points, and broadened with a 2-kHz Gaussian prior to transformation.

Under these conditions, the first two points in the free induction decay (at $t = 0.0$ and at $t = 1.8$ μs) are unavailable in any of our data sets. These points can be filled in via linear prediction (*14*), as long as the number of missing points is small. Moreover, the amplitude accuracy of the zero-time point can be checked independently, as any errors introduce only a frequency-independent offset into the spectrum. (As in all wide-line spectra, small offsets in the initiation of digitization may lead to large phase errors.) Given the high quality of the rest of the data set, and the limited number of missing points, this step proceeds without difficulty or distortion—as can be observed in Fig. 2, which shows the Fourier transform of our reconstructed $\mathcal{S}(j)$.

CONCLUSIONS

We have demonstrated, experimentally and theoretically, that the bandwidth of noise excitation experiments can be extended far beyond what has been previously understood possible in a conventional NMR probe and without substantial spectrometer modifications. This work demonstrates that spectra of arbitrarily broad bandwidth can reliably be reproduced. We expect that the ability to quantitatively measure broad NMR lineshapes, even in the intermediate dynamics limit, will

make it possible to address a broad range of problems previously considered beyond the range of standard Fourier transform NMR technology.

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