



## NOISE Spectroscopy: Applications to Solid State NMR

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Received November 1, 2002

**Abstract:** One of the oldest, still unsolved, and often ignored problems in magnetic resonance remains the issue of how to observe undistorted, normal one-dimensional spectra where the frequencies and their relative intensities represent faithfully the distribution of spins and sites in the sample within the magnet. Often distortions in these parameters are accepted, as the price of sensitivity enhancement, or because it is unclear just how these distortions might be avoided. Surprisingly enough, the problem is exacerbated by the use of modern techniques of pulsed Fourier transform NMR. Noise spectroscopy is an approach to solving the problem of distorted NMR spectra, which is largely under appreciated; it promises virtually “unlimited” distortionless bandwidths without costly hardware investments. Nonetheless, its exploitation remains limited. We will discuss why noise spectroscopy belongs in the arsenal of tricks spectroscopists should be aware of, show examples where its use is essential if accurate, quantitative NMR is to be expected, and discuss some recent approaches which extend its applicability yet further, particularly in solid state NMR and in applications to quadrupolar nuclear spins.

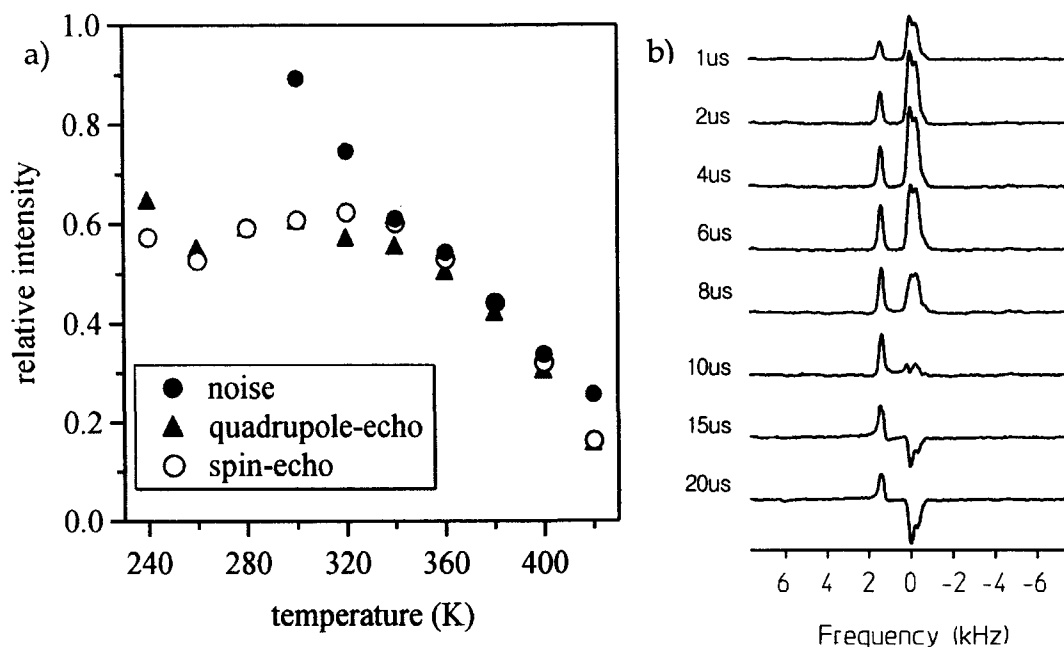
### INTRODUCTION

Since its introduction to magnetic resonance field by Ernst and Kaiser,<sup>1,2</sup> NMR spectroscopy based on the use of incoherent rf irradiation fields, commonly known as stochastic or noise spectroscopy, has brought up only a little interest. Noise spectroscopy is an approach to solving the problem of distorted NMR spectra, which is largely under appreciated; it promises virtually “unlimited” distortionless bandwidths without significant hardware modification. Ernst, Bodenhausen and Wokaun described stochastic excitation as a sleeping beauty for practical applications in their book.<sup>3</sup>

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Most interactions of nuclear spins, whether with neighboring electrons or nuclear spin distributions depend on the orientations with respect to the external magnetic field and on the intra- or inter-molecular distances. While the rapid molecular motions in the liquid state simplify these NMR spectra so as to provide a direct insight into chemical structures, much richer information about the details of molecular orientations and distances between spins is lost, and appears only in rather indirect ways through relaxations.<sup>4</sup> In the solid state, every spin interaction appears superimposed one atop another in the NMR spectrum including all the details of both molecular structure and dynamics, which may unfortunately make a detailed analysis hopeless or at least very difficult. Many methods have been developed and successfully applied in solid state in order to get high-resolution spectra close to those found in liquid state.<sup>5-7</sup> It is, however, not always best to try to get the high-resolution spectra in solid state since both lineshape and linewidth are nonetheless highly informative about molecular orientations, distances and dynamics. In many cases, one interaction dominates other interactions. This is typically the case in deuterium NMR, even though analysis often requires computer simulation. Also it is often possible to extract one main interaction, such as the chemical shift anisotropy<sup>8</sup> or dipole-dipole couplings<sup>9</sup> among all others.

For the general solid applications in magnetic resonance, wide bandwidth of spin response however makes signals disappear quickly due to the broad band of interfering frequencies, and much more pulse power is generally required than in liquid state in order to cover the whole bandwidth. Furthermore, high power pulses are often far from ideal for quadrupolar nuclear spins and actual effect strongly depends on the quadrupolar coupling constant. The inevitable delay after pulses due to the finite receiver and probe recovery time could, therefore, cause significant consequences for normal solid applications. Substantial amount of signal could decay away during the "dead-time" and the spectrum could be easily distorted. In order to overcome this difficulty, spin-echo methods are generally adapted in pulse sequence for solid applications. This may refocus signals after the echo-time, the gap between pulses, so that intact signals is observable even after strong pulses. However, when the molecular dynamics time scale approaches to the spin-echo time ( $\sim 20 \mu\text{s}$ ), as is often found in solid-state materials over broad range of temperatures, the spin resonance frequency changes during the echo-time. As a result, the signal does not refocus after the echo-time, decays even further and the spectrum is distorted. Simulation can be often customized to consider the dynamics effect on dephasing of the signal during the echo time if the dynamics mode is obvious and well known. But, it is certainly far from ideal, and can cause vague interpretation based on the indecisive data. Fig. 1. demonstrates potential distortions that often happen in solid applications; a) dynamics effect on echo sequences when the dynamic time scale is comparable to the echo time, b) dependence of actual response to the pulse effect on the nuclear spin orientation.



**Fig. 1.** a) Relative  $^7\text{Li}$  NMR intensities of a Li-Montmorillonite intercalated with poly(ethyleneoxide) as a function of temperature for quadrupolar echo, spin echo, and noise experiments. Echo sequences show substantial intensity losses between 260 and 320 K where the dynamics time scales come close to the echo time. b)  $^{23}\text{Na}$  NMR MAS spectra of 1:4 mixture of NaCl and  $\text{NaNO}_3$ , obtained with 45 kHz pulse power, and pulse width as specified. The discrepancy of spin responses to the varying pulse width originates from the difference in  $^{23}\text{Na}$  quadrupolar coupling constants of mixture.

Noise excitation methods can be used to obtain true wideband absorption spectrum in solid state—even in the presence of dynamics. Most of the solid applications use high power pulses with the length of longer than 1  $\mu\text{s}$ , which is not strong and short enough for many wide band or quadrupolar nuclei applications. In contrast, many of these demanding applications can be handled better with power as small as milli-watt and shorter pulses as in usual noise-based experiments. Typical noise experiments are performed by applying a series of irradiation sequence with much less power than conventional pulsed experiments. In this paper, we review some of our recent applications of noise spectroscopy in NMR which show that its application range exceed than commonly appreciated; and that at least the one-dimensional applications in solids, which will be the focus of this paper, deserve a more common interest from NMR experimentalist.

### **Basic Theory**

While almost as old as the FT NMR experiment, noise experiments are still unfamiliar to most of NMR spectroscopist. A major complication in understanding NMR experiments based on noise excitations arise from the rather loose connection in the time-sequence between the series of pulses and associated evolving signals. Stochastic or noise-based NMR methods generally do not have any particular restrictions in the pulse power and width, enabling quite general and important set of applications even in multi-dimensional experiments. Our work in this paper will however focus on the weak-pulse limit so that the system response is linear in the experimental input, focusing instead on the important but more limited question of how one might observe the spectrum of a nuclear spin species in a sample which faithfully reproduces the distribution of resonance frequencies found in the sample.

A typical noise experiment is performed by applying a series of irradiation sequence derived from pseudo random numbers, MLBS(maximum length binary sequences), which is designed to provide a uniform excitation over a broad bandwidth,<sup>10</sup> and accumulating one response signal right after each pulse. Such pulse sequences incorporate only pseudo-random  $0^\circ$  and  $180^\circ$  phase shifts, and can be generated from tabulated shift-register based algorithms using exclusive NOR logic. In the weak multi-pulse regime, as in typical noise-based experiment associated with one-dimensional spectroscopy, each pulse in the irradiation sequence with the length of at most a couple degrees is assumed to generate tiny magnetization evolution from the same dynamically equilibrated longitudinal magnetization in the linear response limit, and not to interact with previously evolving transverse magnetization. This is distinctively different perspective in noise experiment from the normal strong pulse experiment, where any sequential pulses interact with any previously evolving magnetizations. As the pulses are typically repeated much faster than relaxation times, they generate simultaneous evolution of lots of small free induction decays, superposed at the top of the previous ones, in what may appear to be useless mess. Thus responses observed in these noise-based experiments have no apparent beginning or ending time in the signal. Nonetheless, there is no unpredictability between the evolution of spin magnetization from numbers of tiny free induction decays evolving mixed all together in time, and the ability to extract the meaningful data because the rules governing the properly chosen inputs and the responses make the deconvolution possible. For the simple one-dimensional applications, this deconvolution can be carried out by the cross-correlation between the series of input irradiation sequence and the responses obtained between pulses. For the multidimensional applications pioneered by Blümich, Ziessow and Kaiser,<sup>11-14</sup> somewhat more complicated data analyses may be required.<sup>15</sup> Under these conditions, all the co-evolving components of transverse magnetization can be separated, recorelated and rephased to yield the familiar free induction decay by cross-correlation of the known input

pulse sequence  $P(l)$  with the measured magnetization  $M(k)$ , which can be carried out mathematically via

$$fid_{R,I}(j) = \sum_i P(i)M_{R,I}(i+j) \quad (1)$$

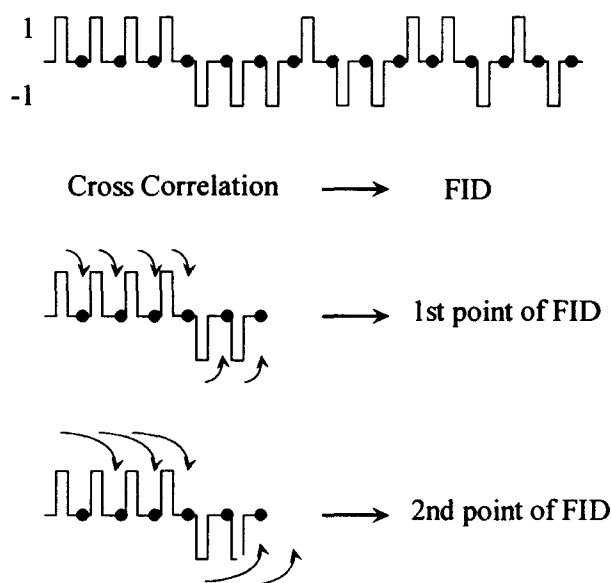
where  $fid_{R,I}(j)$  is the  $j$ th complex data point in the free induction decay,  $M_{R,I}(i+j)$  is the complex magnetization response measured  $j$  time intervals of length  $\tau_p$  after the  $i$ th pulse, and  $P(i)$  is a record of the applied pulse sequence which repeats continuously. For the MLBS sequences,  $P(i) = 1$  or  $-1$  for all  $i$  (representing 0 and 180 degrees, respectively), though for other sequences it may be more involved. The index  $(i+j)$  is cyclic with period  $J$  corresponding to the number of the excitation pulses applied before the whole pseudo-random sequence repeats cyclically; thus, when  $(i+j) \geq J$ ,  $(i+j)$  is replaced by  $(i+j) - J$ . Fig. 2. illustrates 4 bit MLBS sequences for example, 15 number of pulses ( $2^4 - 1 = 15$ ), signal accumulation after each pulse and the graphical process of cross-correlation generating the first two points of more familiar FID. As is well known, the auto-correlation of random numbers generates delta functions, self-cancelling their effects on all over the points except the center point. The characteristics of the pseudo-random number, MLBS, guarantees to collect only the necessary correlations for each FID point, canceling all the other pulses effect at the corresponding time. The effects of the spike at the center points due to the auto-correlation of random numbers can also be easily removed either by adjusting the amplitude of the pulses or by simply correcting the baseline of the spectrum after cross-correlation.

## DISCUSSIONS AND RESULTS

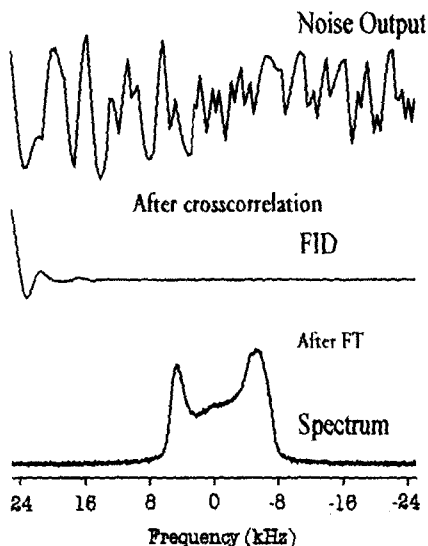
As an example of this procedure we show, in Fig. 3. an actual  $^{23}\text{Na}$  NMR Noise experiment with 10 bit-MLBS sequences for noise excitation and describes the data processing. The noise response output do not illustrate any clue about how to tie with conventional NMR data. It can be of use to generate any meaningful information only by evaluating with the input sequence. The cross-correlation with the excitation sequences reshuffles and phases each of the individual response data, yielding a response function comparable to that observed by strong-pulse methods in similar amounts of averaging time.

An advantage of using noise-excitation for quadrupolar nuclus is demonstrated in Fig. 4., which shows  $^{23}\text{Na}$  Noise/MAS NMR spectra of mixture of NaCl and  $\text{NaNO}_3$ , obtained with only as little as 75 Hz pulse power and pulse width as specified. The quadrupolar coupling constants of the NaCl crystal is close to zero due to the high symmetry of the octahedral cubic structure, on the other hand  $\text{NaNO}_3$  has qcc bigger than MHz. Even with the strongest pulse power currently available, mostly the central transition can be only

excited for nucleus with such large quadrupolar interaction. The actual spin response to the pulse power depends on the magnitude of quadrupolar coupling constant. The linear response limit obtained using very little pulse power as in typically found in noise-based excitation experiment basically removes the dependence on the magnitude of quadrupolar interaction. The difference in  $^{23}\text{Na}$  quadrupolar coupling constants of mixture does not cause any effect on the spin responses with the varying pulse width in noise experiment, but made big divergence with strong pulses as seen in Fig. 1. b).

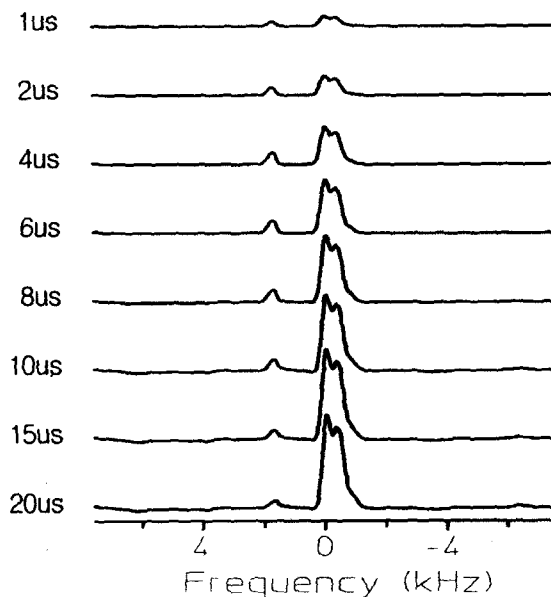


**Fig. 2.** A representative Noise experiment. 15 pulses were generated based on the 4-bit MLBS sequence,  $(2^4 - 1 = 15)$ . Black dots correspond to response signal points accumulated after each pulse. An actual experiment would carry on with large number of cycles with periodic interruptions for phase cycling, using at least 9-bit MLBS sequences. The whole summation of each correlation between the pulses (1 or -1) and the response data at the corresponding positions generate the familiar FID data point at the matching time.



**Fig. 3.**  $^{23}\text{Na}$  Noise NMR in  $\text{NaMnO}_4$ . 10 bit-MLBS sequences were used for noise excitation. Cross-correlation reorganizes noise output and generate a familiar FID.

Once excited, by whichever means chosen, magnetization evolves at its natural frequencies. Each time the transverse magnetization is sampled, it includes all the evolution frequencies which characterize the spin system, and so the sampling requirements in noise spectroscopy are identical to those which characterize “normal” Fourier transform NMR spectroscopy; i.e. where  $\tau_{\text{samp}}$  is the time interval between sampled data points, the Nyquist frequency  $\omega_N$  is precisely  $1/2\tau_{\text{samp}}$ . It is impractical to sample the evolving signal in the presence of an applied field and as a result any noise-based experiment consists of pulses separated by windows adequate to sample the excited and evolving magnetization.<sup>16</sup> In most applications of noise spectroscopy, it appears that a single data point has been sampled for each applied pulse, so that traditionally,  $\tau_{\text{samp}} = \Delta t = 1/2\omega_N$ . Even with the much softer pulses (usually  $\sim 5$  orders of magnitude less than the typical pulse power) in noise experiment, the finite dead-time, however, makes it impossible to open the receiver unit right after each pulse and to get an uncorrupted data point. This inevitable delay before the accumulation of the response data, therefore, limits the sampling rate, and eventually restricts the possible spectral bandwidth, so that even these methods may not always wide enough for applications in solid state. Where probe recovery times are as long as  $5 \mu\text{s}$ , this would appear to limit the available total bandwidth to approximately  $\pm 100 \text{ kHz}$ .<sup>17</sup> No fundamental consideration based in the theoretical treatments, however, would appear to restrict experiments to following this particular experimental detail.



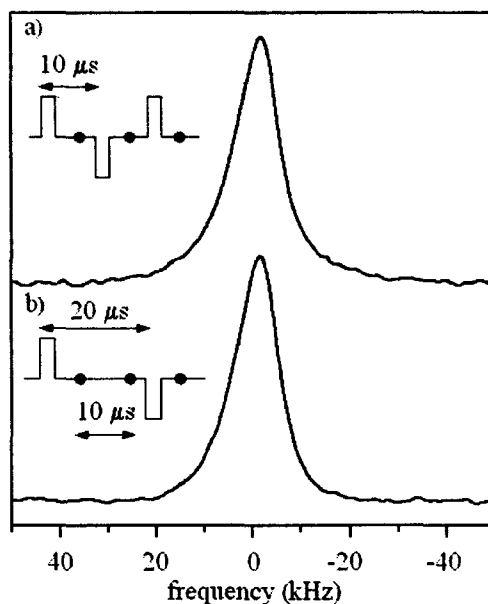
**Fig. 4.**  $^{23}\text{Na}$  Noise/MAS NMR spectra of mixture of  $\text{NaCl}$  and  $\text{NaNO}_3$ , obtained with 10 bit MLBS sequences for noise excitation, with 75 Hz pulse power and pulse width as specified. The difference in  $^{23}\text{Na}$  quadrupolar coupling constants of mixture does not cause any effect on the spin responses with the varying pulse width.

We extended the pulse sequences, by adding pulses of amplitude zero between normal noise pulses, immediately before the additional points of sampled magnetization. This process has no impact on the spectral coverage of the excitation sequence. Of course, where there is no applied field, there is no recovery time required before we sample the magnetization. Fig. 5. demonstrates how we achieve the same spectrum with the same  $\tau_{\text{samp}}$ , and independent of  $\Delta t$ , where we illustrate the essential idea with two spectra of the  $^7\text{Li}$  nuclei found in a sample of Li-montmorillonite/PEO at 300 K. The lineshape is dominated by the interaction of  $\text{Fe}^{3+}$  paramagnetic impurities found in the lattice with the  $\text{Li}^+$  cations which, with the intercalated PEO, occupy the pores. In (a) we show the “traditional” noise spectrum observed with  $\tau_{\text{samp}} = \Delta t = 10 \mu\text{s}$ , while (b) shows the same spectrum after an identical pulse sequence and number of pulses where  $\tau_{\text{samp}} = 10 \mu\text{s}$  and  $\Delta t = 20 \mu\text{s}$ . These set of spectra clearly indicate that there is no need to maintain identical data sampling and pulse rates in one-dimensional spectroscopic applications of noise spectroscopy. This suggests an approach to the faithful reproduction of broad bandwidth spectra without the

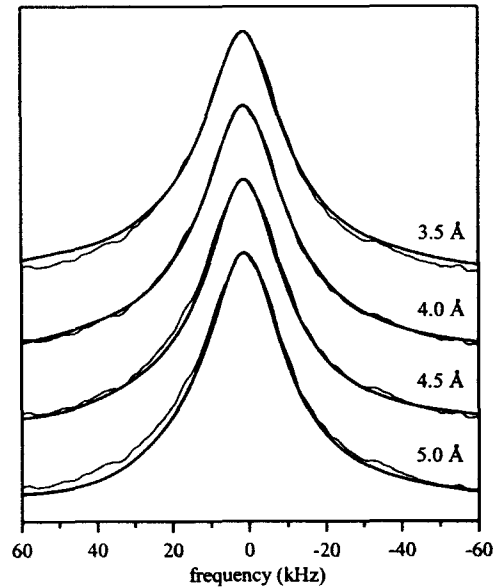


need for NMR spectrometers and probes with deadtimes shorter than  $\tau_{\text{samp}}$ . Noise-based excitation including pulses of amplitude zero can be extended and generalized to obtain bandwidth over than 100 kHz, as shown in Fig. 6, where simulated spectrum matches quite well with the experimental data.

While Figs. 5, 6 suggests that this procedure might be used to generate the free induction decay in a single experiment, this is not generally true. As  $\tau_{\text{samp}}$  is decreased so as to maximize the experimental bandwidth, the sampling time becomes shorter than the ringdown time of the probe and receiver network and some of the sampled data points will overlap with pulses. Under these conditions the cross-correlation calculation creates a corrupted version of the signal function. Nonetheless, it is possible to design a small set of experiments which fill in data points which were missing from earlier experiments. We therefore define a series of  $p$  experiments leading to signal functions  $\{S_1, S_2, \dots, S_p\}$ . In each experiment, we maintain the same  $\tau_{\text{samp}}$ , but vary the pulse spacing  $\Delta t_n$  differ systematically. In each signal record  $S_n$ , gaps which may be several points wide reappear periodically, but each signal functions  $S_n$  has gaps



**Fig. 5.**  ${}^7\text{Li}$  noise-based NMR spectra of Li-montmorillonite with poly(ethylene oxide) intercalated between silicate layers (Li/PEO/MM). Both spectra were accumulated with a 10 bit MLBS sequence and equal numbers of rf pulses. a). One data point is acquired between pulses separated by  $10 \mu\text{s}$ . b). The spectrum observed when two data points are acquired between pulses separated by  $20 \mu\text{s}$ , and cross-correlation with an input sequence where additional pulses of amplitude 0 are included.



**Fig. 6.** Each simulated spectrum of  ${}^7\text{Li}$  is superposed atop the experimental spectrum observed in a Li/PEO/MM sample by noise excitation NMR at 240K with pulses of amplitude zero to expand the observable bandwidth. The best matched spectrum at  $\Delta z = 4 \text{ \AA}$  suggests that Li ions exist  $4 \text{ \AA}$  away from the plane of paramagnetic sites, the surface of silicate layers.

with different period. It is therefore possible to design and combine a set of a few experiments to fill in the gaps together upto certain number of points and truncate the signal functions beyond that point. In Fig. 7, we demonstrate experimentally that our proposal is capable of generating absorption lineshapes for broad line samples based on noise excitation, where we show the temperature-dependent absorption lineshape for deuterated PEO, d-PEO, over a broad temperature range from just below  $T_g$  to just below  $T_m$ . The applied rf power was  $\sim 13 \text{ dBm}$ ,  $\tau_p \approx 500 \text{ ns}$  and  $\tau_{\text{samp}} = 1.8 \mu\text{s}$ , though with such short pulses the shape of the pulse must remain poorly defined. Below  $T_g$ , at 200 K, the spectrum is a characteristically broad Pake powder pattern. Above  $T_g$ , PEO coexists in amorphous and crystalline fractions, which differ substantially in mobility. As the temperature is raised, this difference in mobility is reflected in the coexistence of a broad powder pattern (representing the static, crystalline polymer) with a substantially narrowed component (representing the more mobile amorphous polymer) which we observe most clearly

beginning from 240 K. At 300 K, the Pake-like component has disappeared but the majority of the spectral intensity is still found in a broad, rather featureless absorption band. Echo experiments, however, preferentially sample the immobilized and/or rapidly moving fractions of the sample; partially narrowed components of the spectrum with dynamical correlation times of the order of the pulse spacing are unobservable. This would suggest that efforts to quantify dynamic vs. static fractions using  $^2\text{H}$  spectroscopy are unlikely to provide accurate quantitation unless the time-domain techniques introduced in this paper are employed.

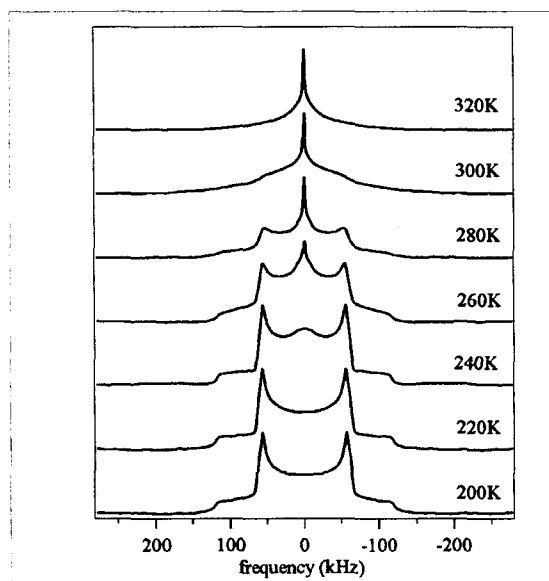


Fig. 7.  $^2\text{H}$  NMR spectra of perdeuterated poly(ethylene oxide), d-PEO, at various temperatures as indicated. Spectra are derived from the series of noise excitation experiments described in Fig. 8. At low T, the Pake powder pattern is observed with excellent reproduction of the static lineshape. At higher temperatures, a broad range of coexistence of static (or slowly mobile) and dynamic fractions are observed as amorphous and crystalline domains coexist above  $T_g$ .

## CONCLUSIONS

We have shown that noise-based experiments first introduced to NMR by Ernst and Kaiser<sup>1,2</sup> nearly 30 years ago are useful in many solid applications which have been largely unappreciated. Noise excitation methods can be used to obtain true wideband absorption spectrum in solid state—even in the presence of dynamics. Many of demanding solid applications has been demonstrated to be feasible even with pulses as weak as a few milliwatts in usual noise-based experiments. The bandwidth of noise excitation experiments has been demonstrated to be extended far beyond what has been previously understood possible, in a conventional NMR probe and without substantial spectrometer modifications.

Recently, it has been shown that probe ring-down effect can be removed by the simple use of composite pulses in noise-excitation NMR experiments.<sup>18</sup> It suggests that even where the ring-down effect is quite large it can be reliably removed, and the technique might be combined with oversampling methods shown in this paper as pulses with amplitude zero, and thus open up the possibility of substantially broad bandwidth. Based on one dimensional solid applications described above, we like to see that more NMR spectroscopist realize that noise-based NMR experiment deserves more appreciation, and implement this techniques for many solid applications ever more.

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