Solid-State Spin-Echo Fourier Transform NMR of ³⁹K and ⁶⁷Zn Salts at High Field

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We have used a two-pulse spin-echo sequence (with appropriate phase cycling) to obtain relatively undistorted second-order powder pattern spectra of the nonintegral spin quad-rupolar nuclei ³⁹K and ⁶⁷Zn, in solids. Using the spin-echo approach, central transition breadths of up to approximately 100 kHz may be readily investigated. Results on 18-crown-6 ether \cdot ³⁹KNO₃ and ³⁹K⁺ · monensin⁻ yield e^2qQ/h values of 1.80 and 3.20 MHz, with $\eta = 0.37$ and 0.52, respectively. For ⁶⁷Zn(OAc)₂ · 2H₂O, $e^2qQ/h = 5.3$ MHz and $\eta = 0.87$ have been obtained. The spin-echo approach should permit investigation of a wide variety of nonintegral spin quadrupolar nuclei in solids using high-field Fourier transform methods. © 1986 Academic Press, Inc.

With the increasing availability of commercial high-field multinuclear NMR spectrometers, more and more nuclei with low gyromagnetic ratios are being investigated (1, 2). However, when one works with low- γ nuclei, "ringing" of the transmitter/ probe circuits and recovery of the receiver frequently results in a spurious broad envelope of frequencies after Fourier transformation, which often completely obliterates the NMR signal (2), especially in solids. In this paper, we report the preliminary results of spin-echo experiments for obtaining relatively undistorted second-order powder pattern lineshapes for the low- γ nonintegral spin quadrupolar nuclei ³⁹K and ⁶⁷Zn, and demonstrate that spectra (for the central, 1/2 to -1/2, transition) having widths of up to approximately 100 kHz may now be obtained, even without any special probe construction, or use of ultra-wideband transmitter (or receiver) electronics.

NMR spectra were obtained on a "home-built" spectrometer at 11.7 T. The pulse sequence used was basically a Hahn echo:

$$(\theta_1)\phi_1 - \tau_1 - (\theta_2)\phi_2 - \tau_2 - (AQ)\phi_3$$
 [1]

using 16-step phase cycling, where the phases of the pulses and receiver were:

$$\phi_1 = xxxx yyyy \bar{x}\bar{x}\bar{x}\bar{x} \bar{y}\bar{y}\bar{y}\bar{y}$$

$$\phi_2 = xy\bar{x}\bar{y} xy\bar{x}\bar{y} xy\bar{x}\bar{y} xy\bar{x}\bar{y}$$

$$\phi_3 = \bar{y}y\bar{y}y \bar{x}x\bar{x}x y\bar{y}y\bar{y} x\bar{x}x\bar{x}$$

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where x, y, \bar{x}, \bar{y} represent 0°, 90°, 180°, and 270° phase shifts, respectively. The intervals τ_1 and τ_2 are the spacings between the two pulses, and the time for echo formation after the second pulse, respectively, and were usually varied between 30 and 70 μ s (although they can be much longer). The phase cycling was designed to cause destructive interference of the free induction decay (FID) tails, but coaddition of the spin-echo signals along x, y, \bar{x} , or \bar{y} and was found to be a particularly good sequence for removal of baseline artifacts from the spin-echo data. The pulse widths used are θ_1 and θ_2 ; θ_1 was typically a 45° or 90° (solid) pulse, and θ_2 was twice the length of θ_1 . The shorter pulse widths are desirable when the overall spectral breadth is very large (up to about 100 kHz for K⁺ · monensin⁻). Note that only the central transition is excited in all cases studied.

We show in Fig. 1A the ³⁹K NMR spectrum of an 18-crown-6 ether \cdot KNO₃ complex obtained using a single (90°, solid) pulse experiment. The severe baseline roll arising from transmitter/probe/receiver "ringing" is obvious, and under such conditions it is not a straightforward matter to simulate the observed spectrum, although the singularities are recognizable. By contrast, we show in Figs. 1B, C, the spin-echo and spin-echo Fourier transform spectrum, using the pulse sequence in [1]. There is no baseline role and a dramatic improvement in lineshape. The expansion of the spectrum is



FIG. 1. 23.33 MHz (11.7 T) ³⁹K spectra of 18-crown-6 ether \cdot KNO₃ complex. (A) One-pulse experiment (pulse width of 7.4 μ s, corresponding to a 90° pulse for the solid), 11,000 scans, 0.2 s recycle time, \pm 71 kHz sweep width (B). Time domain response using the pulse sequence given in [1], first pulse width = 3.7 μ s, second pulse = 7.4 μ s, τ_1 = 1 ms, 25,000 scans, 0.2 s recycle time, \pm 71 kHz sweep width. In this experiment, for demonstrating the suppression of the FID due to the two pulses, data acquisition was begun immediately after the first pulse. The echo-maximum occurs at about 2 ms. (C) Fourier transform of the (half) echo in (B). The unusually large τ_1 value required to suppress all ringing results in a spectrum with a somewhat poorer signal-to-noise ratio than is normally achievable. (D) Expansion of spectrum in Fig. 1C. (E) Simulation of spectrum in Fig. 1D using $e^2 q Q/h = 1.80$ MHz, $\eta = 0.37$ and $\delta_i = 0$ ppm.

shown in Fig. 1D, and an excellent simulation may be obtained, as shown in Fig. 1E, yielding a nuclear quadrupole coupling constant (e^2qQ/h) of 1.80 ± 0.02 MHz, asymmetry parameter (η) of 0.37 ± 0.02 , and isotropic chemical shift (δ_i) of approximately 0 ppm (from 1 *M* KCl). The e^2Qq/h value is somewhat smaller than that reported for 18-crown-6 ether \cdot K⁺ complexes in solution (3), where values of approximately 2.4 MHz were obtained. Good agreement between the results of ¹⁷O spin-echo experiments and those obtained via wide-line ¹⁷O NMR, on Si¹⁷O₂, have also been obtained (data not shown).

We show in Figs. 2A and B the ³⁹K spectrum and its simulation for a system displaying an even larger $e^2 qQ/h$ value than that of the crown ether complex, K⁺ · monensin⁻ (an ionophorous antibiotic), and in Figs. 2C and D, the ⁶⁷Zn spectrum and its simulation for Zn(CH₃COO)₂ · 2H₂O. For K⁺ · monensin⁻ the results of the spectral simulation yield $e^2 qQ/h = 3.20 \pm 0.03$ MHz, $\eta = 0.52 \pm 0.02$, and δ_i approximately 0 ppm from 1 *M* KCl. For Zn(CH₃COO)₂ · 2H₂O the results of the spectral simulation yield $e^2 qQ/h = 5.3 \pm 0.1$ MHz, $\eta = 0.87 \pm 0.03$ and δ_i approximately 0 ppm from 1 *M* Zn(NO₃)₂. Note that in the case of K⁺ · monensin⁻, the second-order



FIG. 2. ³⁹K spectrum of K⁺ · monensin⁻ and ⁶⁷Zn spectrum of Zn(CH₃COO)₂ · 2H₂O at 11.7 T, using the pulse sequence given in [1]. (A) ³⁹K NMR spectrum of potassium complex of monensin at 23.33 MHz with 3.7 and 7.4 μ s pulse widths (corresponding to 45° and 90° pulse widths for the solid), $\tau_1 = 48 \ \mu$ s, $\tau_2 = 62 \ \mu$ s, 200,000 scans, and a recycle time of 0.2 s. (B) Simulation of spectrum in (A) using $e^2 q Q/h = 3.20$ MHz, $\eta = 0.52$ and $\delta_i = 0$ ppm. (C) ⁶⁷Zn NMR spectrum of Zn(CH₃COO)₂ · 2H₂O using 4 and 8 μ s pulse widths (corresponding to 90° and 180° pulse widths for the solid), $\tau_1 = 50 \ \mu$ s and $\tau_2 = 68 \ \mu$ s, 300,000 scans, and a recycle time of 0.2 s. (D) Simulation of spectrum in (C) using $e^2 q Q/h = 5.3$ MHz, $\eta = 0.87$ and $\delta_i = 0$ ppm.

powder pattern is some 85,000 Hz in breadth. Recording such a powder-pattern spectrum without some type of spin-echo sequence would be quite difficult on most NMR spectrometers in the absence of a wideband transmitter or *Q*-damped probe, and our results can undoubtedly be improved upon if pulse-power fall off is taken into account. Similarly, neither "magic-angle" nor "variable-angle" sample spinning would be very effective in causing line-narrowing, since the linewidth is much larger than the highest spinning speeds currently achievable.

We have demonstrated that the spin-echo approach outlined above may in many cases be useful for obtaining relatively undistorted lineshapes for low- γ nonintegral spin quadrupolar nuclei in solids. More detailed experimental, and theoretical analyses are now in order. For higher- γ and larger I nuclei, we believe quite sizeable $e^2 qQ/h$ values should be accessible. For example, for ¹⁷O (I = 5/2, resonance frequency (ν_L) = 68 MHz at 11.7 T, and for $\eta = 0$), $e^2 qQ/h$ values of about 15 MHz should be accessible to study, opening up the possibilities of solid-state NMR of organic compounds (ethers, ketones, etc.). Since in this high-field experiment there are no mechanical sample manipulations involved, there are few restraints on the range of temperature which may be investigated, and sample T_1 values are also relatively unimportant. We thus believe that these, or related, spin echo methods may find widespread application in the investigation of the NMR spectroscopy of a variety of nonintegral spin quadrupolar nuclei in solids.

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