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

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Received February 18, 1986

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 quadrupolar nuclei $^{39}$K and $^{67}$Zn, 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 $^{39}$KNO$_3$ and $^{39}$K$^+$ monensin yield $e^2qQ/h$ values of 1.80 and 3.20 MHz, with $\eta = 0.37$ and 0.52, respectively. For $^{67}$Zn(OAc)$_2$.2H$_2$O, $e^2qQ/h = 5.3$ 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.

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-$\gamma$ 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-$\gamma$ nonintegral spin quadrupolar nuclei $^{39}$K and $^{67}$Zn, 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:

\[(\theta_1)\phi_1-\tau_1-(\theta_2)\phi_2-\tau_2-(\Lambda Q)\phi_3\]

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

\[\phi_1 = xxxx yyyy xxxx yyyy \]
\[\phi_2 = xyyx xyyx xyyx xyyx \]
\[\phi_3 = yyyy xxxx yyyy xxxx \]

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where $x, y, x, \bar{y}$ represent $0^\circ$, $90^\circ$, $180^\circ$, and $270^\circ$ phase shifts, respectively. The intervals $\tau_1$ and $\tau_2$ 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 $\mu$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 $x, y, x, \bar{y}$ and was found to be a particularly good sequence for removal of baseline artifacts from the spin-echo data. The pulse widths used are $\theta_1$ and $\theta_2$; $\theta_1$ was typically a $45^\circ$ or $90^\circ$ (solid) pulse, and $\theta_2$ was twice the length of $\theta_1$. The shorter pulse widths are desirable when the overall spectral breadth is very large (up to about 100 kHz for $K^+\cdot$ monensin$^-\cdot$). Note that only the central transition is excited in all cases studied.

We show in Fig. 1A the $^{39}$K NMR spectrum of an 18-crown-6 ether $\cdot$ KNO$_3$ complex obtained using a single ($90^\circ$, 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) $^{39}$K spectra of 18-crown-6 ether $\cdot$ KNO$_3$ complex. (A) One-pulse experiment (pulse width of 7.4 $\mu$s, corresponding to a 90$^\circ$ 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 $\sim 3.7$ $\mu$s, second pulse $\sim 7.4$ $\mu$s, $\tau_1 = 1$ 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 $\tau_1$ 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 $e^{i\eta Q}/\hbar = 1.80$ MHz, $\eta = 0.37$ and $\delta_1 = 0$ 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 \( 1.80 \pm 0.02 \) MHz, asymmetry parameter \( (\eta) \) of \( 0.37 \pm 0.02 \), and isotropic chemical shift \( (\delta_i) \) of approximately 0 ppm (from 1 M KCl). The \( e^2Qq/h \) value is somewhat smaller than that reported for 18-crown-6 ether - K\(^+\) complexes in solution (3), where values of approximately 2.4 MHz were obtained. Good agreement between the results of \(^{17}\)O spin-echo experiments and those obtained via wide-line \(^{17}\)O NMR, on Si\(^{17}\)O\(_2\), have also been obtained (data not shown).

We show in Figs. 2A and B the \(^{39}\)K spectrum and its simulation for a system displaying an even larger \( e^2Qq/h \) value than that of the crown ether complex, K\(^+\)· monensin\(^-\) (an ionophorous antibiotic), and in Figs. 2C and D, the \(^{67}\)Zn spectrum and its simulation for Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O. For K\(^+\)· monensin\(^-\) the results of the spectral simulation yield \( e^2Qq/h = 3.20 \pm 0.03 \) MHz, \( \eta = 0.52 \pm 0.02 \), and \( \delta_i \) approximately 0 ppm from 1 M KCl. For Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O the results of the spectral simulation yield \( e^2Qq/h = 5.3 \pm 0.1 \) MHz, \( \eta = 0.87 \pm 0.03 \) and \( \delta_i \) approximately 0 ppm from 1 M Zn(NO\(_3\))\(_2\). Note that in the case of K\(^+\)· monensin\(^-\), the second-order

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**Fig. 2.** \(^{39}\)K spectrum of K\(^+\)· monensin\(^-\) and \(^{67}\)Zn spectrum of Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O at 11.7 T, using the pulse sequence given in [1]. (A) \(^{39}\)K NMR spectrum of potassium complex of monensin at 23.33 MHz with 3.7 and 7.4 \( \mu \)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 \( e^2Qq/h = 3.20 \) MHz, \( \eta = 0.52 \) and \( \delta_i = 0 \) ppm. (C) \(^{67}\)Zn NMR spectrum of Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O using 4 and 8 \( \mu \)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 \( e^2Qq/h = 5.3 \) 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 $e^2qQ/h$ values should be accessible. For example, for $^{17}$O ($I = 5/2$, resonance frequency ($\nu_L$) = 68 MHz at 11.7 T, and for $\eta = 0$), $e^2qQ/h$ 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.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation Solid-State Chemistry Program (Grant DMR 83-11339), by the Biophysics Program (Grant PCM 83-02512), and by unrestricted grants-in-aid from the Allied-Signal Company, and by the Mobil Foundation.

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