Single- and Double-Resonance Experiments of Quadrupolar Nuclei in Solids Using Sensitivity Enhancement of the Central Transition

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Population enhancement for NMR of the central transition of quadrupolar nuclei in solids is performed by using adiabatic radiofrequency sweeps of the satellite transitions. Single-resonance experiments are reported for ^{17}O, ^{23}Na, ^{27}Al, and ^{93}Nb nuclei in powders of Al_2O_3, $NaNbO_3$, and $LiNbO_3$ and in Pyrex glass. Experimental techniques using single-coil probe circuits capable of both wideband frequency sweeps and narrowband detection are presented. The combination of population enhancement with cross polarization from ^{27}Al to ^{17}O in α-Al_2O_3 (corundum) powder is demonstrated. The sensitivity-enhancement technique is robust, with no critical parameters. © 1994 Academic Press, Inc.

INTRODUCTION

Half-integer quadrupolar spins are present in many organic, inorganic, and biological solids and have therefore been the subject of numerous nuclear magnetic resonance studies of atomic, electronic, and molecular structure, as well as atomic motions. However, quadrupolar broadening is often quite strong in these systems (1–3), so that many NMR techniques which are applicable to spin-$\frac{1}{2}$ nuclei, such as magic-angle sample spinning, are less effective for quadrupolar nuclei. During the past few years, efforts have been made to find new methods for investigation of such quadrupolar spin systems. For example, line-narrowing techniques such as double-rotation (DOR) (4) and dynamic-angle spinning (DAS) (5–7) have been developed to increase spectral resolution. Double-resonance schemes involving quadrupolar nuclei (8–13) have also been implemented and provide useful information about spin–spin couplings, and thereby about structure. However, because of the broad lines involved, spectral sensitivity is frequently a problem.

We recently proposed and successfully demonstrated a technique for sensitivity enhancement of the central transition (14). In this method, the populations of the $m = \pm I$ Zeeman levels (I = the nuclear spin) are adiabatically trans-

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ferred into the $m = \pm\frac{1}{2}$ levels by means of radiofrequency sweeps. As a result, the population difference of the central levels increases by a factor of $2I$. The effectiveness of this approach was demonstrated with ^{27}Al experiments on α-Al_2O_3 (corundum), in both single-crystal and powder forms (14). To obtain this signal enhancement, there is no need to detect the satellite resonances; only an approximate knowledge of the quadrupole frequency is required. The population-transfer mechanism was subsequently investigated in more detail (15), showing the limits of the approximation in which each satellite resonance is treated as a fictitious spin-$\frac{1}{2}$. In particular, at high RF field strengths and/or slow sweep rates, higher-order transitions ($\Delta m \geq 2$) are excited, and this decreases the efficiency of the sensitivity enhancement.

We report here three new results using this population-transfer method. First, sensitivity enhancement has been applied to a wide variety of systems in both polycrystalline powders and glass. The technique performs well in each case and appears to be quite robust and easy to set up, with no critical parameters, as expected for adiabatic passages. Second, we report new probe circuitry which can be used for both broadband (low-Q) frequency sweeping (to transfer populations into $m = \pm\frac{1}{2}$) and narrowband (high-Q) high-sensitivity detection, which should facilitate applications of the technique. Third, the sensitivity-enhancement technique is combined with cross polarization (CP) between pairs of quadrupolar nuclei, as from ^{27}Al to ^{17}O in α-Al_2O_3.

EXPERIMENTAL

All experiments were performed in an 8.3 T, 89 mm bore magnet (Cryomagnet Systems, Inc., Indianapolis, Indiana). Both a homebuilt spectrometer and a Chemagnetics CMX-360 were employed, depending on the required sweep range. The room-temperature probe designs are discussed below.

Corundum (α-Al_2O_3) powder was from Fisher Scientific (Fair Lawn, New Jersey), while α-$Al_2$$^{17}O_3$ was prepared from [^{17}O]boehmite (16). $NaNbO_3$ and $LiNbO_3$ powders were purchased from CERAC (Milwaukee, Wisconsin).

Dual-Q Probe Circuits

Population transfer from the $m = \pm I$ levels to the $m = \pm \frac{1}{2}$ levels is accomplished by using two RF sweeps (14). The first sweep starts at a higher frequency than the highest satellite resonance frequency and sweeps down, ending just above the central transition. The sweep performs adiabatic inversions on each satellite transition in turn, moving the $m = I$ population eventually to $m = \frac{1}{2}$. A similar adiabatic sweep then transfers the contents of $m = -I$ to $m = -\frac{1}{2}$. Thus the probe must have a usable bandwidth as wide as the entire spectrum (central plus all satellite transitions).

The nth transition frequency ν_n ($n = -4, -3, -2, \ldots, 3, 4$, for $I = \frac{9}{2}$) between the levels $m = n \pm \frac{1}{2}$ is given by first-order perturbation theory. One has

$$\nu_n = \nu_0 + n\nu_Q, \qquad [1]$$

where ν_0 is the Zeeman frequency and ν_Q is the quadrupole frequency. The satellites are inhomogeneously broadened by the angular variation of ν_Q in powders and glasses. Thus, the peak-to-peak bandwidth required is $(2I - 1)$ times the maximum ν_Q.

The original proof-of-principle experiments (14) simply used a probe with an intentionally degraded Q. The sweep enhancement does not require particularly strong RF fields, so low Q is satisfactory for the RF sweeps. However, this method of obtaining the required bandwidth for the RF sweeps greatly reduces the receiving sensitivity. A truly high-sensitivity experiment should have a wide bandwidth for the sweep enhancement and a narrowband, high-Q circuit for signal reception. One solution to this problem is a crossed-coil design, with an inner coil of high Q and good filling factor for reception and an outer, low-Q coil for the RF sweeps. However, it will generally be difficult to retrofit this design to the majority of existing single-coil probes.

Instead, single-coil probe circuits capable of operating with narrow or broad bandwidths are presented in Fig. 1. In Figs. 1a and 1b, overcoupling is employed for wideband operation. In Fig. 1a, the single transmission line to/from the NMR spectrometer's duplexer (T/R switch) is switched with a mechanical coaxial relay (Dow-Key, Santa Barbara, California)—an acceptable solution since switching need not be particularly rapid. The relay coil is driven by a signal from the spectrometer's pulse programmer. For high-Q, high-sensitivity narrowband operation, the relay is deenergized, so the spectrometer is connected to the lower tap point. This point is located by trial and error so that the probe appears as 50 Ω, resistive at this point, and at resonance. For wideband operation, the higher tap point is used. Here, the probe is overcoupled, so the bandwidth is increased. The bandwidth is increased (decreased) by raising (lowering) the tap point. In this design, the 50 Ω output impedance of the transmitter serves to load and "de-Q" the probe, and no physical, power-
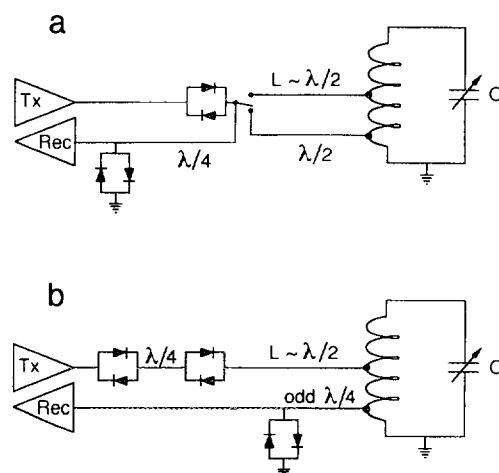

FIG. 1. Single-resonance probe circuits used for RF-sweep sensitivity enhancement. (a) Coaxial relay allows switching between the matched, high-Q port and the overcoupled, low-Q port. (b) Low-Q/wideband port is connected to the transmitter; the matched coupling port (high-Q, narrowband) is only for signal reception. By avoiding mechanical relays, faster switching and greater reliability result by use of (b).

dissipating resistor is required. For the same bandwidth and transmitter power, the present scheme yields $2^{1/2}$ more B_1 (RF amplitude) than an impedance-matched design with an explicit Q-spoiling resistor.

It should be noted that the output impedance of many power amplifiers varies with the power output level. In addition, if the output impedance is not equal to the characteristic impedance of the transmission lines, the length of the line between power amplifier and probe affects the bandwidth. However, despite these potential drawbacks, we find that the overcoupled method works very well.

The high-Q port of the probe can be tuned for minimum reflected wave in the usual way. The low-Q port is never impedance-matched, however. Tuning of the low-Q port is performed with a small pickup coil to monitor B_1, while the probe is driven with a swept-frequency source.

The use of cables of approximately $\lambda/2$ length allows the coaxial relay to be located outside the NMR magnet. The open ends of the "unused" cables present nearly infinite impedances to the probe coil taps. The probe tuning capacitor, C, is adjusted first to center the low-Q port's response function (using the pickup coil) at the NMR frequency, ν_0. Then the resonance frequency of the high-Q port is brought into coincidence (ν_0) by small changes in the cable length, L. Thereafter, final tuning changes are made simply by varying C to obtain minimum reflected wave from the high-Q port. Because the cables have relatively low standing-wave voltages and currents, they do not measurably degrade probe performance. In particular, the Q at the high-Q port is not found to be decreased by the upper cable of length L. Furthermore, the exact length of the lower cable in Fig. 1a is

not critical, because this line is connected to such a low tap point on the coil.

The design shown in Fig. 1a allows the high-Q port to be used for both reception and excitation of the central transition. The scheme in Fig. 1b always uses the low-Q port for excitation (frequency sweeping and pulses applied to the central transition) and the high-Q port for signal reception. An advantage of this method is that a mechanical relay is not required, being replaced by crossed diodes. This is useful for systems with short T_1 and for greater reliability with long signal averaging (many relays are specified at only several million operations). An extra crossed diode set with an intervening approximately $\lambda/4$ line reduces the bleed-through of noise from the power amplifier during reception. Unless a large B_1 is needed in order to cover the central line, the approach in Fig. 1b is the simplest. Tuning follows the procedure described above.

The use of tapped inductors reduces the number of high-voltage components in the probe. The two-tap circuit also has the advantage that the tuning is not affected to first order by the change in coupling. The overall approach of using two values of the RF coupling to obtain two bandwidths should be applicable with other circuitry as well.

Cross-Polarization Experiments

The double-resonance probe used for the ^{27}Al to ^{17}O CP was based on the circuit described in Ref. (17). Since the Q of both channels was about 160, we degraded the Q of the ^{27}Al channel to about 60 ($\sim$1.5 MHz bandwidth) to allow for a $\pm$720 kHz frequency sweep. The lower Q was achieved with a 16 Ω resistor in series with the high-frequency matching capacitor and before the low-frequency trap (17).

RESULTS AND DISCUSSION

Single-Resonance Experiments

Results for the ^{17}O sweep-enhanced NMR of $\sim$10% ^{17}O-enriched corundum powder are shown in Fig. 2. Each ^{17}O NMR spectrum was obtained by Fourier transformation of a single spin echo. The selective $\pi/2$ and π pulses had durations of 15 and 30 μs, respectively. The delay between the pulses was 30 μs, with acquisition starting 30 μs after the last pulse. The RF amplitude, measured on an aqueous AlCl$_3$ solution, was 5.5 kHz. The spectrum in Fig. 2a shows the sweep-enhanced result, with the spin-echo sequence preceded by the RF sweeps. Since ^{17}O in corundum has a maximum quadrupole frequency, ν_Q, of about 325 kHz ($\eta = 0.55$) (18), we used frequency sweeps starting $\pm$730 kHz above/below resonance. Then, the frequency was decremented/incremented by 800 Hz every 10 μs, to about $\pm$20 kHz from ν_0. The RF amplitude during the sweep was about 2.8 kHz. The time between both sweeps was 1 ms, and the spin-echo se-
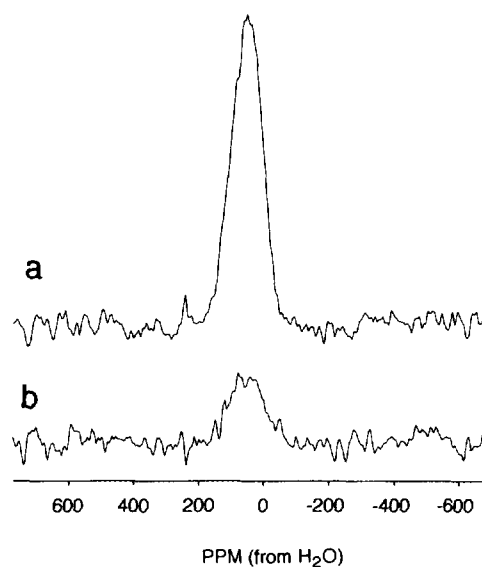

FIG. 2. Oxygen-17 central transition Fourier-transformed spectra of 10% enriched corundum powder at 48 MHz, obtained from a spin-echo sequence (15 and 30 μs pulses; pulse separation, 30 μs) at an RF amplitude of 5.5 kHz. (a) The spin echo was preceded by two RF-sweep pulses: $\pm$730 to $\pm$20 kHz offset; 8.8 ms each; RF amplitude, 2.8 kHz. (b) The spin echo without RF sweep. Both spectra are single-scan experiments.

quence started 5 ms after the sweep. The probe circuit used was that in Fig. 1a.

Theoretically, for $I = \frac{5}{2}$, we expect a maximum sweep enhancement of 5. Experimentally, we find 4.7 $\pm$ 0.7 in Fig. 2, in good agreement with theory. Also, as we reported earlier for ^{27}Al in corundum (14, 15), the sweep enhancement is not very sensitive to the sweep rate or to the RF amplitude.

The spin–lattice relaxation time of ^{17}O, with excitation of only the central transition, was about 360 s. The effective T_1 is longer for experiments such as the RF-sweep enhancement, which perturb the populations of all the levels (14). This effect diminishes somewhat the practical gain in signal-to-noise for sweep enhancement, which must involve consideration of the rate of signal averaging. However, a second set of RF sweeps which occurs within T_1 will yield additional signal. If we assume thermal equilibrium populations of a spin-$\frac{5}{2}$ system as 5, 3, 1, -1, -3, and -5 (for $m = \frac{5}{2}, \frac{3}{2}, \ldots, -\frac{5}{2}$, respectively), immediately after sweep enhancement, the population numbers will be 3, 1, 5, -5, -1, and -3 (14). Now, assuming the subsequent central transition experiment cancels the $m = \pm\frac{1}{2}$ population difference (e.g., a selective $\pi/2$ pulse), the populations (after T_2) will be 3, 1, 0, 0, -1, and -3. A second sweep enhancement will change the populations to 1, 0, 3, -3, 0, and -1. Another $\pi/2$ pulse on the central transition will yield an FID of relative amplitude 3 (where unity is the thermal equilibrium signal). Thus, after the first FID is acquired, one can still obtain additional signal from the system, without waiting for spin–lattice relaxation. For spin-$\frac{5}{2}$, coaddition of the two FIDs in such a doubly

enhanced method yields a theoretical signal-to-noise (S/N) improvement of $(5 + 3)/\sqrt{2} = 5.66$, only a small improvement over 5.0. However, for $I = \frac{9}{2}$ (e.g., ^{93}Nb), the first three FIDs have relative amplitudes 9, 7, and 5. Thus, coaddition results in a S/N improvement of $(9 + 7 + 5)/\sqrt{3} = 12.1$, noticeably better than the factor of 9 for a singly enhanced FID.

Since the ^{17}O T_1 in the corundum sample is long (360 s), multiple sweep enhancements are readily achieved in times less than T_1. Three successive sweep enhancements were performed, with the spin system initially at thermal equilibrium. The time delays for the second and third sweep enhancements were about 2 s, $\ll T_1$. Each sweep enhancement was followed by a selective $\pi/2$-π echo sequence, and the spin-echo amplitude was measured. We found relative echo amplitudes of 4.7, 3.0, and 1.5, in reasonable agreement with the theoretically expected 5, 3, and 1.

For ^{93}Nb in LiNbO$_3$ powder, we expect from the central transition linewidth a maximum ν_Q of about 800 kHz. Thus, the total spectral width according to Eq. [1] is 6.4 MHz. By overcoupling the coil, a bandwidth of about 10 MHz was obtained. Because T_1 of the ^{93}Nb is about 100 ms, the probe circuit in Fig. 1b was used. The elimination of the slow-switching relay is helpful with the shorter T_1.

The homebuilt spectrometer was used for the wide frequency sweeps by replacing the frequency synthesizer with an FM generator driven by a digital-to-analog converter in the computer. The maximum signal enhancement for a single spin-echo was 6 ± 1 (Fig. 3a), substantially less than the ideal value of 9. We believe this difference is due to the short T_1. Indeed, the maximum enhancement resulted with ± 3.2 MHz sweeps in a total of 15 ms and with the maximum available RF amplitude of 5.5 kHz. Wider sweep ranges, faster or slower sweeps, or weaker RF all decreased the enhancement, suggesting that the above conditions are barely adiabatic, and any lengthening of the process results in further losses due to T_1. Although the signal enhancement for a single experiment was only 6, the results nevertheless demonstrate the effectiveness of the sweep-enhancement method even under unfavorable conditions, such as a very wide first-order linewidth and short T_1.

For the ^{23}Na resonance in NaNbO$_3$, a signal enhancement of 2.7 ± 0.5 was obtained, in accord with the expected factor of 3 (data not shown).

Spin echoes from ^{27}Al in Pyrex (a borosilicate glass) are presented in Fig. 3b, with and without sweep enhancement. Here, the maximum enhancement was 3 ± 0.5, in contrast to the ideal factor of 5. The enhanced spin echo also exhibits a change in lineshape. The relatively small signal enhancement for the glass is not understood, since nutation experiments (3) on the same sample suggest a more or less unique maximum quadrupole frequency for ^{27}Al of about 800 kHz (data not shown). The range of frequencies swept was ± 2.2
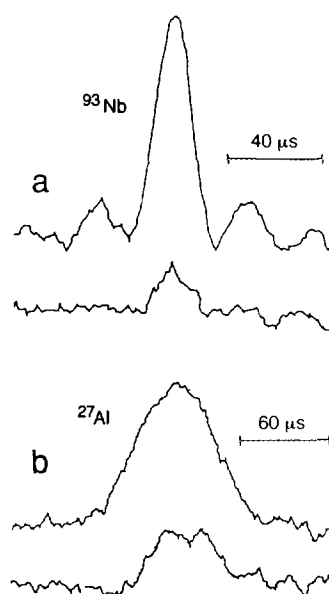

FIG. 3. Niobium-93 and aluminum-27 NMR spin echoes with and without RF-sweep sensitivity enhancement. (a) ^{93}Nb NMR of LiNbO$_3$, at 86.57 MHz. The top spectrum is sweep-enhanced, while the bottom one is without sweep enhancement. (b) ^{27}Al NMR of a borosilicate (Pyrex) glass, at 92.27 MHz. Other conditions as given for (a).

MHz; a further increase in the sweep width did not change the enhancement.

Cross-Polarization Experiments

Using the CMX-360 spectrometer, we first repeated the ^{27}Al to ^{17}O CP reported previously (17), with similar results. Then the single-resonance ^{27}Al population-transfer (sweep-enhancement) parameters were optimized to yield an enhancement of 4.2 ± 0.5. Starting ± 730 kHz above/below resonance, the frequency was decremented/incremented by 800 Hz every 10 μs to about ± 20 kHz from ν_0. The maximum ^{27}Al enhancement was found for repetition times longer than 150 s, although the apparent T_1 of the ^{27}Al for selective excitation of the central transition was only about 2 s! In fact, the effective T_1 determined from the sweep-enhanced ^{27}Al (single-resonance) intensities was about 50 s, a value found for similar experiments on single crystals of pure α-Al$_2$O$_3$ (14). This behavior suggests that the impurities which cause fast relaxation upon selective excitation of the central transition ($T_1 = 2$ s for the present sample, compared with 12 s for the single crystal) are not effective for the satellite transitions. Such a finding is not unexpected, since the presence of impurities will slightly change the quadrupole coupling of the ^{27}Al nuclei. This will broaden the satellite transitions and inhibit spin diffusion in the satellites, but not in the central transition (19).

The overall pulse scheme for the CP experiment is shown in Fig. 4. The RF amplitudes during sweeping were chosen
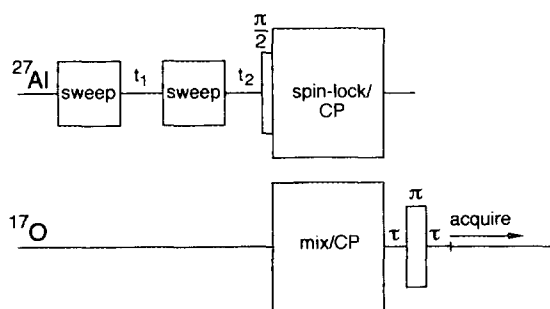
FIG. 4. Schematic of the pulse sequence used for CP combined with RF-sweep enhancement; $t_1 = 1$ ms, $t_2 = 5$ ms, $\tau = 30$ μs.
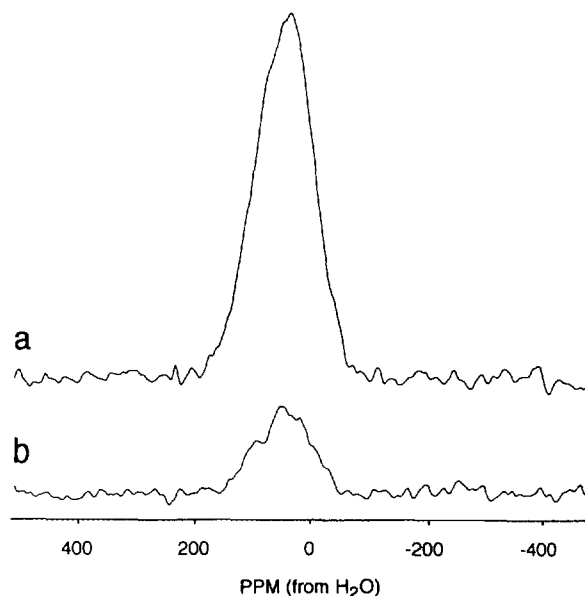

FIG. 5. Oxygen-17 CP spectra of $\sim 10\%$ ^{17}O-enriched corundum powder, at 8.3 T. (a) Sweep enhancement of the ^{27}Al prior to CP; 64 acquisitions. (b) Without sweep enhancement of ^{27}Al; 128 acquisitions. The display gains have been normalized for the different numbers of acquisitions. The repetition time was 200 s in both cases.

to be about 3.3 kHz. The time between both sweeps was 1 ms. The ^{27}Al-selective $\pi/2$ preparation pulse had the same RF amplitude and started 5 ms after the end of the second sweep. The spin-lock pulse, 90° phase shifted with respect to the preparation pulse (RF amplitude of about 10 kHz for both resonances), started immediately after the preparation pulse. The refocusing ^{17}O-selective π pulse (3.3 kHz) started 30 μs after the end of the mix pulse. Finally, ^{17}O data acquisition commenced 30 μs after the π pulse. The ^{27}Al spins were not decoupled during data acquisition. The same CP time constant (dependence on mixing pulse duration) was measured with and without sweep enhancement, $T_{IS} \approx 8$ ms (data not shown). ^{17}O CP spectra obtained with and without sweep enhancement of ^{27}Al are shown in Fig. 5. A signal enhancement of 4.5 ± 0.5 was observed. Because for the CP only the ^{27}Al central transition is spin-locked, an ideal increase in the ^{17}O signal amplitude of a factor of 5 is predicted, close to the experimental result.

In previous experiments it was shown (17) that the efficiency of the quadrupole-to-quadrupole CP in α-Al$_2$O$_3$ is only about 30%; nevertheless, a significant signal enhancement of ^{17}O can be obtained, due to the difference in spin-lattice relaxation times between ^{17}O and ^{27}Al. With sweep enhancement of ^{27}Al, the effective ^{27}Al T_1 is longer. Thus, the question of the actual improvement in S/N arises. Data are presented in Fig. 6 comparing the ^{17}O signal amplitudes in the ^{27}Al–^{17}O CP experiment, with and without prior sweep enhancement of the ^{27}Al, as a function of the experimental repetition time, T. The sweep-enhanced ^{17}O CP signal depends strongly on T, while the unenhanced CP signal is nearly constant for $T \geqslant 5$ s. Because the ^{27}Al central transition effective T_1 is ~ 2 s, this last result is expected. With sweep enhancement, the ^{17}O CP signal attains full amplitude only for $T \geqslant 200$ s, in approximate accord with the effective T_1 (50 s) of the sweep-enhanced ^{27}Al single resonance (see above). With the measured enhancement factor of 4.5, the S/N of the unenhanced ^{17}O CP signal with $T = 5$ s and the enhanced CP ^{17}O signal at $T = 200$ s will be comparable, in equal experimental times.

All of the experiments reported here and in earlier work (14, 15) have been on static samples. For a sample spinning about the magic axis, ν_Q will be time dependent, passing through zero two or four times on each rotation. While this produces interesting passage effects (adiabatic or otherwise) (9, 10), we know of only one way to apply the present scheme to spinning samples. That is, one should use $\theta = 0$ (spinning axis along the external field and ν_Q time independent) for the sensitivity enhancement and then flip the spinning axis to the magic angle for data acquisition. This would be particularly easy to implement in an existing DAS experiment (5–7).
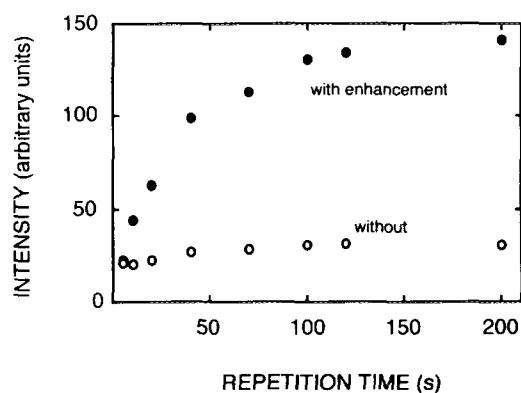

FIG. 6. Repetition time dependence of the ^{17}O signal intensity for ^{27}Al to ^{17}O CP experiments with ($\bullet$) and without ($\bigcirc$) RF-sweep enhancement of the ^{27}Al spins.

CONCLUSIONS

Enhancement of the central transition intensity for half-integer spin quadrupolar nuclei has been successfully applied to several polycrystalline powders and a glass. With the dual-Q single-coil circuits reported here, the method is easy to implement and yields a significant signal-to-noise enhancement. There are no critical parameters associated with the frequency sweep. The maximum quadrupole frequency need be known only very approximately; the satellite resonances need not be detected.

CP experiments demonstrate that, as anticipated, the sweep enhancement can be combined with CP for studies of spin–spin couplings.

ACKNOWLEDGMENTS

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