6798 *J. Am. Chem. Soc.* **1996,** *118,* 6798−6799

Wide-Line ^{14}N NMR in Solids and Reorientation-Induced Redistribution of Isochromats

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Received March 8, 1996

Nitrogen is an important element in all branches of chemistry, including biological, environmental, polymer, and materials chemistry. Although the quadrupolar ^{14}N isotope ($I = 1$) has a high natural abundance (99.6%), there are relatively few ^{14}N NMR studies in the solid state. A low magnetogyric ratio ($^1/_{14}$ that of the proton) may be partially responsible for this neglect; however, the primary reason is the sizeable magnitude of the nuclear quadrupole coupling constants (NQCC) found for nitrogen atoms in all but the most symmetrical (tetrahedral) environments, whose estimated median value is ca. 3−4 MHz.[1,2] Consequently, pulsed ^{14}N NMR studies of the fundamental transitions ($\Delta m = 1$) in the energy level diagram shown in Figure 1 have been limited either to powders exhibiting relatively small NQCC values, typically 10−200 kHz,[3] or to single crystals, where sharp lines are observed instead of powder patterns.[4] Overtone ^{14}N NMR, in which weakly-allowed $\Delta m = 2$ transitions are observed,[5] has been explored as a means of overcoming some of these limitations.[6] However, it is difficult to extract the parameters of interest from overtone spectra of powders and, in particular, to obtain accurate NQCC values. We demonstrate in this communication that it is possible to obtain pulsed ^{14}N NMR spectra from polycrystalline solids having large NQCC values by selectively observing fundamental transitions, i.e. for a given ^{14}N electric field gradient (efg) tensor orientation either the transitions $0 \rightleftharpoons +1$ or $0 \rightleftharpoons -1$, *but not both*. Such transitions can be described in terms of a *fictitious spin-$^1/_2$ formalism*.[7,8] Broad ^{14}N NMR powder pattern spectra can be obtained by the stepped-frequency approach;[9] the example we show employs a pulse train sequence to increase the detection sensitivity. Since only a small fraction of the spins in the sample have the proper orientation to be detected at any one time, unusual effects result from reorientation-induced redistributions of isochromats. We describe a new experiment that utilizes these effects to improve the sensitivity of detection.

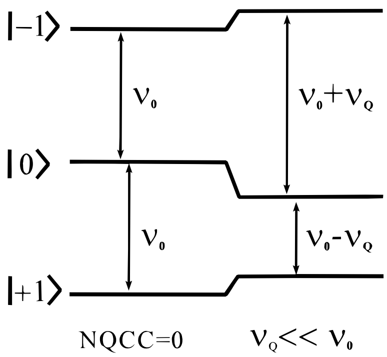

Figure 1. Energy-level diagram of $I = 1$ spin system in high magnetic field for zero and nonzero NQCC values (from first-order perturbation theory). The states are indicated at left by their m_z values. Arrows depict fundamental transitions at the Larmor frequency ν_0 and (with scale exaggerated) at frequencies differing slightly by ν_Q, the quadrupolar interaction for a particular orientation of efg tensor.

The vast majority of pulsed NMR studies of $I = 1$ nuclei have involved the ^{2}H nucleus, whose NQCC is at most ca. 250 kHz. As a result of the relatively small NQCC values, these studies have almost invariably utilized nonselective excitation, with the rf carrier frequency set at the center of a symmetrical quadrupolar powder pattern and having sufficient strength to excite the high- and low-frequency transitions symmetrically placed to either side of center. For the much larger NQCC values typical of ^{14}N, however, such an approach is not feasible. The limiting factor is not only the rf field strength achievable, but also the probe bandwidth (in our experiments about 250 kHz). However, if the three-level system of Figure 1 is *selectively* irradiated such that the radiofrequency is resonant with only two of the three levels, the $I = 1$ spin response can be described in an operator subspace describing rotations of a fictitious spin-$^1/_2$ nucleus.[7,8] The effective rf field in this subspace is scaled by a factor of $\sqrt{2}$, resulting in an effective $\pi/2$ pulse length that is 71% of that in the nonselective case. Furthermore, the fictitious spin-$^1/_2$ behavior implies that a conventional Hahn spin echo ($(\pi/2)_x-\tau-(\pi)_{x \text{ or } y}-\tau-$observe) is appropriate, rather than the quadrupolar echo typically used for ^{2}H NMR.[10]

We have chosen powdered potassium nitrate (KNO_3) for our initial experiments. Its NQCC (751 kHz) and asymmetry parameter η (0.022) are known from a single-crystal ^{14}N NMR study.[11] A selective $\pi/2$ pulse length of 8.3 μs at the ^{14}N Larmor frequency of 21.6 MHz (at 7.05 T) was calculated from nonselective observation of the signal from ammonium chloride in a 10 mm solenoidal coil. The Hahn spin-echo signal from KNO_3 yielded a half-height width in the frequency domain of ca. 40 kHz, resulting from the limited rf strength. To increase the sensitivity of detection, we use trains of $(\pi)_y$ pulses separated by intervals of 2τ, with multiple data points acquired around each midecho. Although this pulse sequence corresponds to the Carr−Purcell−Meiboom−Gill (CPMG) sequence familiar from solution-state NMR, it evokes a different type of spin system behavior in the present situation. The decay time of the echo train is *not* the same as that we measure from a single Hahn echo with variable τ intervals (20 ms). Rather, it is a considerably longer time whose value depends upon the pulse spacing and which reflects a type of spin-locking behavior in the rotating frame.[12] For the shortest τ values used (120 μs), we were able to coadd 512 individual echo signals and thereby obtained a 20-fold enhancement in the signal:noise.

To obtain the ^{14}N powder pattern spectrum, we use a stepped-frequency method.[9] In this approach, a broad spectrum is obtained by summing frequency-domain spectra acquired at uniformly-spaced frequency intervals, after correction for the different offsets. Superposition in the frequency domain yields a frequency resolution superior to that obtained by simply representing each frequency offset by its integrated signal

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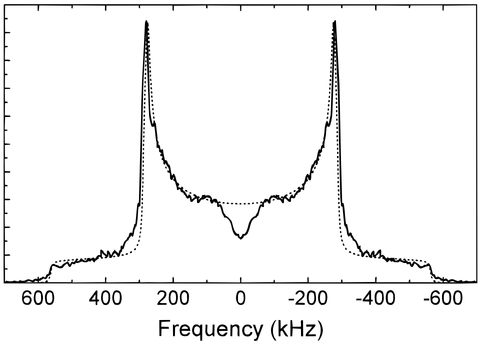

Figure 2. ^{14}N NMR stepped-frequency spectrum of KNO_3 (solid line) and theoretical simulation[17] (dotted line). Magnitude spectra obtained from coadded Fourier-transformed (without apodization) echoes in a pulse train at 33 distinct frequency intervals were used to construct this spectrum. The measured spin−lattice relaxation time T_1 of 40 s led to the choice of a relaxation delay of 50 s. See text for further details.

intensity and is thus better able to reveal sharp features in the powder-pattern spectrum. To obtain the spectrum of KNO_3, frequency offsets of 20 kHz were used to satisfy the necessary criteria for this method.[9] The probe and transmitter amplifier were retuned every 60 kHz. In this way, frequency ranges much larger than the probe or amplifier bandwidths can be covered.[13] The high-frequency side of the KNO_3 powder pattern was reflected about the center frequency to give the spectrum shown in Figure 2.[14] The spectrum agrees well with that calculated from the values NQCC = 751 kHz, $\eta = 0.022$ (dashed line), with a line broadening of 7.5 kHz applied. The intensities appear to be faithfully represented except near the center of the spectrum, where the excitation is not selective. The slight discrepancy in the splitting of the horns is attributed to neglect of the small second-order correction in this simulation.[5a] Four days were required to obtain this spectrum, which has a good signal:noise ratio. The sensitivity will increase considerably at higher magnetic field strengths. One reason is that the shorter dead times at higher frequencies will allow shorter pulse train intervals. The effects of an increased Boltzmann population difference and higher Larmor frequency can be estimated by assuming a $B_0^{7/4}$ dependence for the signal:noise ratio;[15] equivalent spectra should be obtainable at 17.6 T in less than $^1/_{25}$ the time.

There is a unique aspect of these experiments associated with the fact that we observe only a small portion of the entire powder pattern at any one time, namely that portion arising from those crystallites whose efg tensors are oriented to resonate at or near the carrier frequency. Rotating the sample (e.g. about an axis perpendicular to the main magnetic field) in general causes new crystallites not saturated by the rf pulses to be brought into resonance at the constant observation frequency. This allows shorter repetition rates since the "heating" of the spins is distributed more evenly. It is desirable to have the rotation period be somewhat longer than the spin−lattice relaxation time T_1, so that the spins are largely relaxed by the time they are observed again. The optimal pulse repetition interval is one just sufficient to enable a saturated group of spins to move outside of the region where they have just been excited. This interval decreases roughly as the ratio of the width of the excited region to the entire width of the powder pattern. This shorter repetition interval leads directly to a gain in sensitivity; *the improvement should be greatest for the broadest powder patterns, just as needed*. Results of this reorientation-induced redistribution of isochromats experiment (which we dub RotIsseRIe) are shown in Figure 3. Pulsing a static sample of KNO_3 yields no discernible signal (bottom trace), whereas pulsing a sample that is slowly rotating at 1 rpm about an axis perpendicular to the magnetic field yields a strong signal (top trace). We estimate that there is a gain in signal:noise by a factor of 2.6 when *both* spectra are obtained with optimal pulse intervals, corresponding to a savings in time of a factor of 7 for the RotIsseRIe case. We are developing a quantitative analysis of the sensitivity gain that considers the relation of frequency space to angular position and rotation.[16]

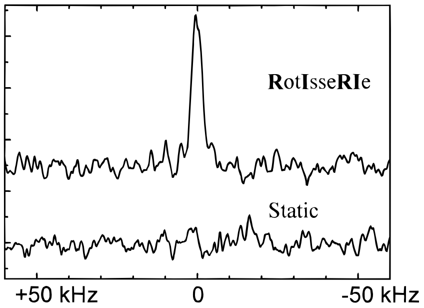

Figure 3. ^{14}N NMR spectra of a 30 mm o.d. tightly-packed sample of KNO_3, near the high-frequency "horn," obtained by Fourier-transformation of a spin-echo, 128 scans, 2 s recycle delay. (Top trace) RotIsseRIe experiment, sample rotating at 1 rpm about an axis perpendicular to the main field via a pair of bevel gears in the probe head connected by a shaft to a synchronous motor beneath the magnet. (Bottom trace) Static sample. Note the substantial gain in signal intensity in the RotIsseRIe experiment.

In summary, the selective excitation of fundamental transitions, the use of pulse trains, the stepped-frequency approach, and the effect of reorientation-induced redistributions of isochromats described in this communication should also have valuable applications to wide-line ^{2}H NMR experiments, as well as to other nuclei. In addition to the external motion imposed upon the sample in the RotIsseRIe experiment, redistributions of isochromats can also take place via *intrinsic* molecular motions leading to reorientation of the efg tensors. We are currently investigating these molecular dynamics effects.

Acknowledgment. This work was supported in part by the Office of Naval Research. E.A.H. is a NRL/NRC Postdoctoral Associate. Helpful discussions with Dr. Allen Garroway, Dr. Joel B. Miller, and Dr. Kenneth McGrath of the Naval Research Laboratory are gratefully acknowledged.

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(13) The size of NQCC that can be observed is limited only by the inverse proportionality of the signal:noise ratio to the powder pattern width, assuming frequency-dependent characteristics of the hardware (such as the *Q* of the NMR probe circuit) are taken into account.

(14) We ignore the slight asymmetry due to the chemical shift anisotropy of the nitrate group (ca. 4 kHz) described in: Bastow, T. J.; Stuart, S. N. *Chem. Phys. Lett.* **1991,** *180,* 305−309.

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