

# $^{14}\text{N}$ Chemical Shifts and Quadrupole Coupling Constants of Inorganic Nitrates

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The isotropic chemical shift and the nuclear quadrupole coupling constant for  $^{14}\text{N}$  were obtained for 14 inorganic nitrates by solid-state MAS NMR measurements at two different field strengths, 9.4 and 11.7 T. The compounds studied were polycrystalline powders of  $\text{AgNO}_3$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{CsNO}_3$ ,  $\text{KNO}_3$ ,  $\text{LiNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{NaNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{RbNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ , and  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . Even though the spectra show broadening due to  $^{14}\text{N}$  quadrupole interactions, linewidths of a few hundred hertz and a good signal-to-noise ratio were achieved. From the position of the central peaks at the two fields, the chemical shifts and the nuclear quadrupole coupling constants were calculated. The chemical shifts for all compounds studied range from 282 to 342 ppm with respect to  $\text{NH}_4\text{Cl}$ . The nuclear quadrupole coupling constants range from 429 kHz for  $\text{AgNO}_3$  to 993 kHz for  $\text{LiNO}_3$ . These data are compared with those available in the literature. © 2002 Elsevier Science (USA)

**Key Words:**  $^{14}\text{N}$ ; NMR; MAS; polycrystalline; inorganic nitrate.

## INTRODUCTION

In the solid-state NMR for half-integer nuclei, the central transition  $|I, 1/2\rangle \rightarrow |I, -1/2\rangle$  is unaffected by first-order quadrupole broadening, but is broadened by the second-order effect (*I*). There are several approaches to obtain solid-state spectra with sufficiently narrow linewidth from half-integer quadrupole nuclei. Most of the methods involve sample spinning, including double angle rotation (2) and variable angle spinning (3); the use of multiple-quantum transition with magic-angle spinning (MAS) (4) can also help to reduce line broadening. For nuclei with integer spins, there is no central transition, and the  $|I, 1\rangle \rightarrow |I, 0\rangle$  and  $|I, 0\rangle \rightarrow |I, -1\rangle$  transitions are affected by both first- and second-order quadrupole broadening.

Nitrogen is one of the most important elements in nature, and exists in numerous inorganic and organic compounds. However, nitrogen NMR (5) suffers from two basic problems:  $^{15}\text{N}$  ( $I = 1/2$ , 0.4% natural abundance) has very low sensitivity and often requires the use of enriched samples;

$^{14}\text{N}$  ( $I = 1$ , >99% natural abundance) has a nuclear quadrupole moment, which is a disadvantage for high-resolution NMR. In dealing with polycrystalline materials, line-narrowing methods for half-integer spins are not efficient for  $^{14}\text{N}$ . Some solid-state  $^{14}\text{N}$  NMR studies have been performed using single crystals, because sufficiently narrow lines can be observed (6–11). Overtone spectroscopy (12, 13) takes advantage of the  $|I, 1\rangle \rightarrow |I, -1\rangle$  transition not being broadened by first-order quadrupole interactions, but second-order broadening and chemical shift anisotropy still present problems for polycrystalline solids (13).

Conventionally it was considered that, because of the presence of large quadrupole splitting, the use of magic-angle spinning to observe the fundamental transitions is not expected to yield useful information for  $^{14}\text{N}$  NMR of polycrystalline material. However, it has been shown recently that this is not necessarily a general situation (14). The basic features of MAS  $^{14}\text{N}$  NMR have been established in this laboratory (15, 16). Recently the simple MAS approach has been greatly improved both experimentally and in data analysis (17).

The goal of this work is to test the method previously proposed (16) for the determination of  $^{14}\text{N}$  chemical shifts and nuclear quadrupole coupling constants simultaneously by carrying out the experiments at two different magnetic fields, without the analysis of spinning sidebands. Simple broadband MAS probes rather than specially designed high-*Q* transmission-line-tuned low-frequency probes (17) were used for the  $^{14}\text{N}$  NMR study of 14 polycrystalline inorganic nitrates. The reason for choosing inorganic nitrates in this study is that their moderate quadrupole coupling constants (~0.4–1.0 MHz) make it possible to observe the  $^{14}\text{N}$  peaks without difficulty. For compounds with quadrupole coupling constants  $\geq 3$  MHz, the second-order broadening makes it extremely difficult to detect the  $^{14}\text{N}$  signals.

## GENERAL CONSIDERATIONS

For the inorganic nitrates studied, homonuclear dipole–dipole interactions can be neglected, and only  $^{14}\text{N}$  quadrupole effects perturb the Zeeman energy levels. Considering the perturbation up to second order, it was shown (16) that the position of the

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central peak,  $\nu^i$ , at the magnetic field  $B_0^i$  can be expressed as

$$\nu^i = \nu_{\text{cs}}^i + \nu_{\text{q}}^i, \quad [1]$$

where the chemical shift contribution  $\nu_{\text{cs}}^i$  is proportional to the magnetic field  $B_0^i$  and, therefore, the Larmor frequency  $\omega_0^{(i)}$ ,

$$\nu_{\text{cs}}^i = (1 - \delta) \omega_0^{(i)} / 2\pi, \quad [2]$$

and the second-order quadrupole shift  $\nu_{\text{q}}^i$  is inversely proportional to the field:

$$\nu_{\text{q}}^i = f \omega_{\text{q}}^2 (3 + \eta^2) / 4\pi \omega_0^{(i)}. \quad [3]$$

In Eq. [3], the factor  $f$  is the ratio between the powder-averaged second-order shift and the maximum shift caused by the second-order quadrupolar interaction,  $\eta$  is the asymmetry parameter, and  $\omega_{\text{q}}$  is related to the quadrupole coupling constant  $\chi = e^2 q Q / h$  by

$$\omega_{\text{q}} = \frac{\pi \chi}{2} = \frac{e^2 q Q}{4\hbar}. \quad [4]$$

As described previously (16), second-order shifts averaged by MAS lie between  $35/49 \approx 0.71$  and 1 of the maximum second-order shift, and the experimental values of  $f$  are close to the middle of this interval,  $f \approx 0.85$ . It should be pointed out that this method of averaging the contribution of the second-order effect is a simplified approach. A more comprehensive analysis depends on the simulation of the lineshapes of different spinning sidebands over a fairly large spectral range (17), which was published after the work described here had been completed.

When the peak position is measured at two different magnetic fields and denoted as  $\nu^1$  and  $\nu^2$ , respectively, a set of two simultaneous linear equations is obtained. Solving this set of equations in terms of the resonance frequencies  $\nu_0^1 = \omega_0^{(1)} / 2\pi$  and  $\nu_0^2 = \omega_0^{(2)} / 2\pi$  leads to expressions for the chemical shift and the quadrupolar coupling constant:

$$\delta = 1 - \frac{\nu^1 \nu_0^1 - \nu^2 \nu_0^2}{(\nu_0^1)^2 - (\nu_0^2)^2}, \quad [5]$$

$$f \omega_{\text{q}}^2 = \frac{8\pi^2 \cdot \nu_0^1 \nu_0^2 (\nu^2 \nu_0^1 - \nu^1 \nu_0^2)}{(3 + \eta^2) [(\nu_0^2)^2 - (\nu_0^1)^2]}. \quad [6]$$

Thus, if the values  $\nu^1$  and  $\nu^2$  can be measured and the factor  $f$  is known, the isotropic chemical shift  $\delta$  and the quadrupole coupling constant  $\chi$  can be determined from the MAS experiments.

Recently, using a specially designed high- $Q$  probe for low-frequency nuclei, Jacobsen and co-workers were able to observe all spinning sidebands in a spectral range of 1 MHz (17). By careful simulations of the lineshapes of the spinning sidebands, they were able to obtain both  $\delta$  and  $\chi$  at a single resonance

frequency. A comparison of the present results with theirs will be presented.

## EXPERIMENTAL

The experiments were carried out on a Varian VXR-500S spectrometer (11.7 T) and on a Varian UNITY/INOVA 400 spectrometer (9.4 T). The resonance frequency for  $^{14}\text{N}$  was 36.124 and 28.892 MHz, respectively.

For both spectrometers the same broadband MAS probe manufactured by Doty Scientific Inc. was used. Because the  $^{14}\text{N}$  resonance frequencies are outside the normal tuning range of the probe, it was modified by the manufacturer for the 11.7-T field, and a homemade tuning rod was used for the 9.4-T field. Since the probe was manufactured to fit the 11.7-T magnet, a PVC bushing was added to the probe to make it fit the 9.4-T magnet for corresponding experiments.

It was shown previously that the exact setting of the magic angle is critical for  $^{14}\text{N}$  MAS NMR experiments (16). However, this could not be done in a single experimental setting due to imperfection in the mechanics of the probe. Therefore, a lever was attached to the tuning screw of the rotor so that the angle could be changed in steps of about  $0.01^\circ$ . Several experiments were performed for every sample by changing the angle in a stepwise manner and taking one spectrum at each setting. When the splitting of the observed resonance peak was at a minimum, the spectrum was assigned to be that at the magic angle (16). To further reduce the uncertainty, a computer program was written to find the "center of mass" of the peak as the exact position of  $\nu^i$ .

All of the compounds in this study were obtained commercially. They were ground into fine powders. Each powdered sample was carefully mixed with 2% (wt) ammonium chloride, the signal of which was taken as the reference peak. The mixed powders were tightly packed in 5-mm (o.d.) thin-wall zirconia rotors. Because  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{LiNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{RbNO}_3$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ , and  $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  are very hygroscopic, they were dried in vacuum at room temperature for about 24 h. No further contact with air was allowed, and the packing was done in a dry bag.

## RESULTS AND DISCUSSION

Fourteen inorganic nitrates were studied at 9.4 and 11.7 T. The MAS spectra are similar to those published previously (15, 16), and the positions for the central peak are listed in Table 1. From these data, the chemical shift was calculated directly using Eq. [5]. The results are given in Table 2. Corresponding values determined from single-crystal studies were found in the literature for only three nitrates (10), and our data are quite close to these values. The recent data obtained from the MAS study of six polycrystalline nitrates (17) are also listed. It can be seen that the chemical shift data obtained from all three methods agree with each other quite well. Although a number of studies on  $^{15}\text{N}$  chemical shifts of organic compounds have been done, very few

**TABLE 1**  
Positions of the <sup>14</sup>N NMR Peaks (Relative to Solid NH<sub>4</sub>Cl) at Two Fields

Nitrate	Peak position/Hz	
	At 9.4 T	At 11.7 T
AgNO <sub>3</sub>	10, 226 ± 50	12, 564 ± 50
Al(NO <sub>3</sub> ) <sub>3</sub>	10, 795 ± 50	12, 887 ± 50
Ba(NO <sub>3</sub> ) <sub>2</sub>	10, 980 ± 50	13, 120 ± 50
Ca(NO <sub>3</sub> ) <sub>2</sub>	10, 723 ± 50	12, 767 ± 50
CsNO <sub>3</sub>	11, 013 ± 50	13, 137 ± 50
KNO <sub>3</sub>	11, 276 ± 50	13, 465 ± 50
LiNO <sub>3</sub>	10, 777 ± 50	12, 290 ± 50
Mg(NO <sub>3</sub> ) <sub>2</sub>	10, 516 ± 50	12, 226 ± 50
NaNO <sub>3</sub>	10, 893 ± 50	13, 028 ± 50
Pb(NO <sub>3</sub> ) <sub>2</sub>	10, 301 ± 50	12, 567 ± 50
RbNO <sub>3</sub>	11, 196 ± 50	13, 335 ± 50
Sr(NO <sub>3</sub> ) <sub>2</sub>	10, 723 ± 50	12, 899 ± 50
Th(NO <sub>3</sub> ) <sub>4</sub> · 4H <sub>2</sub> O	10, 251 ± 50	12, 333 ± 50
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O	10, 312 ± 50	12, 362 ± 50

studies on solid inorganic nitrates have been published. Of the few known to us (18–20), the values are also quite close to the <sup>14</sup>N data listed in Table 1 (for example, the value for NaNO<sub>3</sub> was found to be 334 ppm in Ref. 19).

The chemical shifts for <sup>14</sup>N cover a range of over 1300 ppm, three times as much as <sup>13</sup>C (5). This wide range of <sup>14</sup>N shifts is due to the relatively large electronegativity of nitrogen, its ability to form multiple bonds, and its potential to stabilize lone pairs. Using solid ammonium chloride as a reference, they range from more than 1000 ppm for certain diazenes to –100 ppm for some silylamines. The chemical shifts of the inorganic nitrates are in the middle of this scale at about 330 ppm. Even though their structures and metal cations are quite different, the variation of their chemical shifts is small. This gives evidence that the <sup>14</sup>N chemical shift is mainly governed by contributions from the nitrate group itself.

The nitrate group carries a single negative charge and is essentially planar, with all oxygen atoms being equivalent. The <sup>14</sup>N chemical shift in inorganic nitrates is determined by three major factors: inductive effects due to the electron-withdrawing ability of the electronegative oxygen atoms, the resonance contribution to the paramagnetic term (2I), and deshielding caused by the cations in the lattice. The data in Table 2 show that the deshielding effect is smallest for Li<sup>+</sup> and Mg<sup>2+</sup>; however, Al<sup>3+</sup> has an even smaller radius and higher charge, but the chemical shift of aluminum nitrate is close to those of other nitrates. Therefore, we have not been able to discern any trend for the chemical shift values in the inorganic nitrates studied.

To calculate the nuclear quadrupole coupling constants from the peak positions, the value of *f* (Eq. [6]) is needed. If it is assumed that this parameter has the same value for all compounds, it can be determined by comparing the experimental data with the nuclear quadrupole coupling constants obtained from single-crystal measurements. This is possible because for small asymmetry parameters ( $\eta < 0.5$ ) the factor  $1/(3 + \eta^2)$  can be approximated by 1/3 within the experimental error (16). Since the <sup>14</sup>N quadrupole coupling constant of a compound depends on the crystalline phase, the following considerations were made in the data treatment.

For potassium nitrate, the nuclear quadrupole coupling constant of Bastow and Stuart (22) was used because it was much newer than the value given by Gourgji (7). For barium nitrate the same argument was used to chose the values given by Weiden Weiss (9) instead of Gourdji (7). However, the value reported more recently (10) was not used because its large deviation from the previous data indicates that the compound studied might be in a different phase. The value for uranyl nitrate given by Whitehouse *et al.* (6) is for the hexahydrate, but only two water molecules are bound to the complex (23, 24) and the others are further away and do not have a large contribution to the field gradient. We considered that, within the experimental error, the value for the hexahydrate can be used for the trihydrate that we

**TABLE 2**  
Quadrupolar Coupling Constants and Chemical Shifts

Nitrate	$\chi$ /kHz ± 10%	Literature values	$\delta$ /ppm ± 20 ppm	Literature values
AgNO <sub>3</sub>	429	466 (10)	337	344 <sup>a</sup>
Al(NO <sub>3</sub> ) <sub>3</sub>	713		327	
Ba(NO <sub>3</sub> ) <sub>2</sub>	711	651 (9) 650 (17)	333	352 <sup>a</sup> 340 (17)
Ca(NO <sub>3</sub> ) <sub>2</sub>	731		322	
CsNO <sub>3</sub>	726		333	
KNO <sub>3</sub>	726	751 (19) 746 (17)	342	342 (17)
LiNO <sub>3</sub>	993		282	
Mg(NO <sub>3</sub> ) <sub>2</sub>	877		293	
NaNO <sub>3</sub>	702	745 (8) 740 (17)	332	338 (17)
Pb(NO <sub>3</sub> ) <sub>2</sub>	510	539 (7,17) 653 (10)	333	348 <sup>a</sup> 334 (17)
RbNO <sub>3</sub>	743		337	
Sr(NO <sub>3</sub> ) <sub>2</sub>	651	609 (8) 614 (17)	332	338 (17)
Th(NO <sub>3</sub> ) <sub>4</sub> · 4H <sub>2</sub> O	639		318	
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O	629	608 (6)	316	

<sup>a</sup> Taken from Ref. (10), converted to NH<sub>4</sub>Cl(s) as reference.

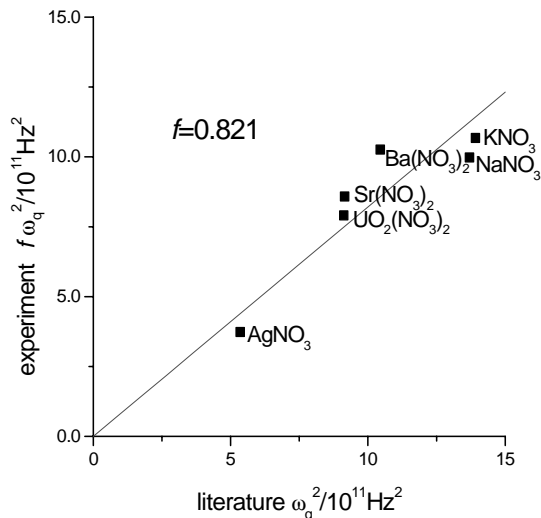


FIG. 1. Correlation between experimental values of  $f\omega_q^2$  (calculated from Eq. [6]) and literature values of  $\omega_q^2$ .

studied. The two nuclear quadrupole coupling constants for lead nitrate reported in the literature (7, 10) are very different from each other. It is suspected that the crystal structures are different in the two cases, and the data were not included in the comparison. We had also carried out experiments with ammonium nitrate, which has a phase transition from phase IV to III at 32°C (18, 25). Because the rotor heated up slightly above room temperature during the experiment, the results were affected by this phase transition and therefore not included.

With these considerations, the values of  $f\omega_q^2$  for seven compounds were calculated using Eq. [6], and then plotted against the corresponding values of  $\omega_q^2$  obtained from the literature (Fig. 1). Fitting the data to a straight line with a zero intercept yields a slope of  $f = 0.821$ , which is very close to the value of  $f = 0.85$  that we estimated previously (16). Thus, the nuclear quadrupole coupling constants of all the compounds studied were calculated by using the value of  $f = 0.821$  in Eq. [6], and the values are listed in Table 2. The values show general agreement with those determined from single-crystal measurements and from the analysis of MAS sidebands, but the percentage deviations are larger than those for the chemical shift data. This is most likely due to the inaccuracy in the value of  $f$ , which was assumed to be the same for all compounds and determined from the correlation plot in Fig. 1.

In contrast to the chemical shifts, the nuclear quadrupole coupling constants show a much greater variation, indicating that the lattice contribution to the values of the nuclear quadrupole coupling constant must play a more important role than for the chemical shifts. In fact, the nuclear quadrupole coupling constant is even affected by defects of a crystal lattice (26). For  $^{14}\text{N}$ , nuclear quadrupole coupling constants normally range from 1 to 5 MHz (27), and the values for the 14 nitrates studied are at the low end of this scale. The nitrate ion itself creates a field

gradient that would give rise to a nuclear quadrupole coupling constant well above 1 MHz (10, 28, 29). However, the field gradient of the lattice partially compensates that effect. As a result, all the nitrates studied have quadrupole coupling constants below 1 MHz. Apparently, the compensating field gradient which acts at the  $^{14}\text{N}$  nucleus is less pronounced for the small ions  $\text{Li}^+$  and  $\text{Mg}^{2+}$  than for the large ions  $\text{Pb}^{2+}$  and  $\text{Ag}^+$ , but there is no general trend observed. In a detailed theoretical calculation of quadrupole coupling constants, it may be possible to take into account the contribution of the counterions in the nearest neighbors of the nitrate ion to the field gradient, but this is beyond the scope of the present work.

In summary, it has been shown that the  $^{14}\text{N}$  nuclear quadrupole coupling constants and chemical shifts of polycrystalline material can be determined by carrying out MAS NMR experiments at two different field strengths. Because of the extreme sensitivity of the quadrupole broadening to the settings of the magic angle, experimentally this method is practical for compounds with quadrupole coupling constants only in the range of about 1 MHz. The chemical shift data obtained are dependable because they do not depend on the choice of the parameter  $f$  (Eq. [5]), but the accuracy of the quadrupole coupling constants is less than that obtained from single-crystal measurements and from a more elaborate numerical method based on the simulation of the lineshapes of a set of spinning sidebands (17). However, the simulation of lineshapes obtained at a single resonance frequency requires knowledge of the chemical shift tensor. Using the present approach, namely carrying out the experiment at two or more magnetic fields (30), it may be possible to eliminate this requirement, so that the more elegant method of lineshape analysis would yield dependable data without using assumed values of chemical shift anisotropy.

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#### REFERENCES

1. A. Abragam, "The Principles of Nuclear Magnetism," Oxford Univ. Press, Oxford (1985).
2. A. Samoson, E. Lippmaa, and A. Pines, High-resolution solid-state NMR. Averaging of second-order effects by means of a double-rotor, *Mol. Phys.* **65**, 1013–1018 (1988).
3. E. W. Wooten, K. T. Muller, and A. Pines, New angles in nuclear magnetic resonance sample spinning, *Acc. Chem. Res.* **25**, 209–215 (1992).
4. L. Frydman and J. S. Harwood, Isotropic spectra of half-integer quadrupolar spins from bidimensional magic-angle spinning NMR, *J. Am. Chem. Soc.* **117**, 5367–5368 (1995).
5. J. Manson, Nitrogen NMR, in "Encyclopedia of NMR" (D. M. Grant and R. K. Harris, Eds.), p. 3222, Wiley, Chichester, UK (1996).
6. B. A. Whitehouse, J. D. Ray, and D. J. Royer, Nitrogen-14 nuclear magnetic resonance of some solid nitrates, *J. Magn. Reson.* **1**, 311–326 (1969).
7. M. Gourdji, These de Doctorat, No. 991, CNRS No. AO 7416, Universite de Paris Sud Orsay (1972).

8. M. Gourdji, L. Guibe, and A. Peneau, Temperature dependence of the nitrogen-14 quadrupole coupling constant in sodium nitrate as studied by NMR on a single crystal, *J. Phys. (Paris)* **35**, 497–508 (1974).
9. N. Weiden and A. Weiss, Nitrogen-14 and barium-137 NMR in single crystals of barium nitrate, in “Magnetic Resonance Related Phenomena, Proc. Congr. AMPERE 18-th (1974),” Vol. 1, pp. 257–258, North-Holland, Amsterdam (1975).
10. R. A. Santos, P. Tang, W.-J. Chien, S. Kwan, and G. S. Harbison, NMR resolution of a crystallographic controversy: Nitrogen-14 single-crystal studies of silver, barium and lead nitrates, *J. Phys. Chem.* **94**, 2717–2721 (1990).
11. T. J. Bastow and S. N. Stuart, Nuclear magnetic shielding tensor of nitrogen-14 in the nitrate ion: Potassium nitrate, *Chem. Phys. Lett.* **180**, 305–309 (1991).
12. R. Tycko and S. J. Opella, Overtone NMR spectroscopy, *J. Chem. Phys.* **86**, 1761–1774 (1987).
13. L. Marinelli, S. Wi, and L. Frydman, A density matrix description of  $^{14}\text{N}$  overtone nuclear magnetic resonance in static and spinning solids, *J. Chem. Phys.* **110**, 3100–3112 (1999).
14. G. Jeschke and M. Jansen, High-resolution  $^{14}\text{N}$  solid-state NMR spectroscopy, *Angew. Chem. Int. Ed.* **37**, 1282–1283 (1998).
15. K. Ermolaev and B. M. Fung, High-resolution  $^{14}\text{N}$  NMR in polycrystalline solids, *J. Chem. Phys.* **110**, 7977–7982 (1999).
16. A. K. Khitrin and B. M. Fung,  $^{14}\text{N}$  nuclear magnetic resonance of polycrystalline solids with fast spinning at or very near the magic angle, *J. Chem. Phys.* **111**, 8963–8969 (1999).
17. H. J. Jacobsen, H. Bildsoe, J. Skibsted, and T. Giavani,  $^{14}\text{N}$  MAS NMR spectroscopy: The nitrate anion, *J. Am. Chem. Soc.* **123**, 5098–5099 (2001).
18. K. L. Anderson-Altmann and D. M. Grant, A solid-state  $^{15}\text{N}$  NMR study of the phase transitions in ammonium nitrate, *J. Phys. Chem.* **97**, 11096–11102 (1993).
19. P. J. Barrie, C. J. Groombridge, J. Mason, and E. A. Moore, Nitrogen-15 nuclear magnetic shielding tensors in nitrite and nitrate ion. Experimental and theoretical determinations, *Chem. Phys. Lett.* **219**, 491–496 (1994).
20. B. V. Schonwandt and H. J. Jakobsen, Phase transitions in  $\text{KNO}_3$  studied by variable-temperature  $^{15}\text{N}$  magic-angle spinning NMR spectroscopy, *J. Solid State Chem.* **145**, 10–14 (1999).
21. M. Hesse, H. Meier, and B. Zeeh, “Spectroscopic Methods in Organic Chemistry,” Thieme, Stuttgart (1997).
22. T. J. Bastow and S. N. Stuart, Nitrogen-14 and potassium-39 nuclear quadrupole coupling in potassium nitrate, *Z. Naturforsch. A: Phys. Sci.* **45**, 459–463 (1990).
23. J. E. Fleming and H. Lynton, Crystal structure of uranyl nitrate hexahydrate, *Chem. Ind. (London)*, 1416–1417 (1960).
24. J. R. Ferrado and A. Walker, Comparison of the infrared spectra of the hydrates and anhydrous salts in systems  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{Th}(\text{NO}_3)_4$ , *J. Chem. Phys.* **45**, 550–553 (1966).
25. J. Selinger, V. Zagar, and R. Blinc, Nitrogen-14 NQR study of the structural phase transitions in ammonium nitrate, *Z. Phys. B: Condens. Matter* **77**, 439–443 (1989).
26. M. H. Cohen and F. Reif, “Quadrupole Effects in Nuclear Magnetic Resonance Studies in Solid State Physics” (F. Seitz and D. Turnbull, Eds.), 2nd ed., Vol. 5, p. 321, Academic Press, London (1957).
27. E. A. C. Lucken, “Nuclear Quadrupole Coupling Constants,” Academic Press, New York (1969).
28. H. M. Maurer, P. C. Schmidt, and A. Weiss, Electric field gradients in the ionic crystals sodium nitrite, sodium tetrafluoroborate, sodium nitrate, and barium nitrate, *J. Mol. Struct.* **41**, 111–130 (1977).
29. M. G. Gibby, R. G. Griffin, A. Pines, and J. S. Waugh, High-resolution NMR of nitrogen-15 in solids, *Chem. Phys. Lett.* **17**, 80–81 (1972).
30. B. C. Schmidt, T. Riemer, S. C. Kohn, H. Behrens, and R. Dupree, Different water solubility mechanisms in hydrous glasses along the Qz–Ab join: Evidence from NMR spectroscopy, *Geochim. Cosmochim. Acta* **64**, 513–526 (2000).