

¹⁴N MAS NMR Spectroscopy: The Nitrate Ion

Hans J. Jakobsen,* H. Bildsøe, J. Skibsted, and T. Giavani

Instrument Centre for Solid State NMR Spectroscopy
Department of Chemistry, University of Aarhus
DK-8000 Aarhus C, Denmark

Received January 2, 2001

Revised Manuscript Received March 7, 2001

Great efforts have been exercised during the past few years in applying magic-angle spinning (MAS) NMR spectroscopy to the highly abundant ¹⁴N quadrupolar nucleus (99.6% natural abundance, spin $I = 1$) in polycrystalline solids.^{1–3} Obviously a successful outcome of these efforts would be highly appreciated in particular if the resulting spinning sideband (ssb) spectra would be of sufficient quality to allow analysis in a straightforward manner, thereby yielding useful spectral parameters. For example, this could involve the procedures and versatile software programs already developed for the analyses of spinning sideband spectra (the complete manifold and/or individual ssb line shapes) for half-integer spin ($I = 3/2, 5/2, 7/2, \dots$) quadrupolar nuclei and ²H.^{4–10} The potential of a routine determination for the ¹⁴N quadrupole coupling constant (C_Q) and asymmetry parameter (η_Q) from such spectra would constitute a valuable parameter set characterizing the environment of the nitrogen atom in addition to the isotropic/anisotropic ¹⁵N chemical shift data, oftentimes determined using ¹⁵N-labeled material.^{11,12} However, for the low- γ ¹⁴N nucleus, and in particular for nitrogens with $C_Q > 0.5$ MHz such as in nitrates, the reported MAS spectra^{2,3} do not appear useful or of sufficient quality for extraction of the quadrupole coupling parameters (and possible chemical shift anisotropy) from computer simulations/optimizations. There are a number of reasons contributing to the experimental difficulties and thus to the hitherto low interest in ¹⁴N MAS NMR. Some of these (e.g., the question of wideband excitation/detection in MAS NMR) are considered in our earlier MAS NMR studies of half-integer quadrupoles,^{4–8} while others have been addressed in the recent papers by Fung et al.^{2,3} It is our experience, however, that a successful outcome of ¹⁴N MAS experiments is highly related to the quality of the MAS probe used for the observation of this low- γ nucleus.

Here we address a number of important issues which greatly improve the experimental aspects of ¹⁴N MAS NMR pursued using the latest generation of high-Q transmission-line tuning MAS probes. Thereby, this work demonstrates the significant progress achieved for the observation and spectral simulation of the complete manifold of ssbs in ¹⁴N MAS NMR spectra for different nitrates. The results clearly represent state-of-the-art ¹⁴N MAS NMR spectroscopy and open the door for a number of applications of ¹⁴N MAS NMR to many areas of chemistry.

* Address correspondence to this author.

- (1) Jescheke, G.; Jansen, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1282.
- (2) Ermolaev, K.; Fung, B. M. *J. Chem. Phys.* **1999**, *110*, 7977.
- (3) Khitrin, A. K.; Fung, B. M. *J. Chem. Phys.* **1999**, *111*, 8963.
- (4) Jakobsen, H. J.; Skibsted, J.; Bildsøe, H.; Nielsen, N. C. *J. Magn. Reson.* **1989**, *85*, 173.
- (5) Skibsted, J.; Bildsøe, H.; Jakobsen, H. J. *J. Magn. Reson.* **1991**, *92*, 669.
- (6) Skibsted, J.; Nielsen, N. C.; Bildsøe, H.; Jakobsen, H. J. *J. Magn. Reson.* **1991**, *95*, 88.
- (7) Skibsted, J.; Nielsen, N. C.; Bildsøe, H.; Jakobsen, H. J. *Chem. Phys. Lett.* **1992**, *188*, 405.
- (8) Kristensen, J. H.; Bildsøe, H.; Jakobsen, H. J.; Nielsen, N. C. *J. Magn. Reson.* **1991**, *92*, 443.
- (9) Massiot, D.; Bessada, C.; Coutures, J. P.; Taulelle, F. *J. Magn. Reson.* **1990**, *90*, 231.
- (10) Bak, M.; Rasmussen, J. T.; Nielsen, N. C. *J. Magn. Reson.* **2000**, *147*, 296.
- (11) Anderson-Altmann, K. L.; Grant, D. M. *J. Phys. Chem.* **1993**, *97*, 11096.
- (12) Duncan, T. M. In *Principal Components of Chemical Shift Tensors: A Compilation*, 2nd ed.; Farragut Press: Chicago, 1994.

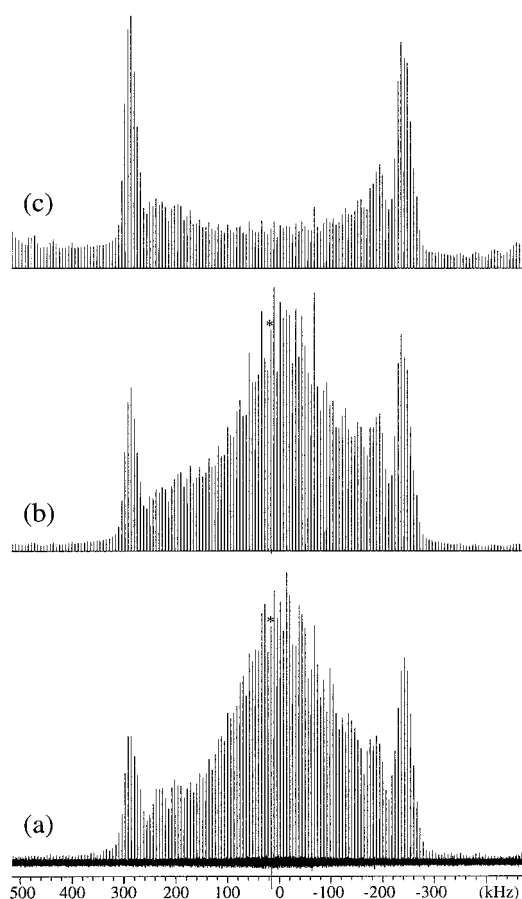


Figure 1. ¹⁴N MAS NMR spectra of the NO₃⁻ ion in KNO₃. (a) Experimental spectrum recorded at 43.34 MHz on a Varian INOVA-600 spectrometer with a 14.1 T widebore magnet using a Varian/Chemagnetics specially designed broadband low- γ frequency 7.5 mm T3 CP/MAS probe ($Q \sim 200$) with transmission-line tuning and a maximum specified spinning speed of 7 kHz. The spinning speed is stabilized to <0.05 Hz (see text) using the Varian/Chemagnetics MAS speed controller. The spectrum was recorded using a spinning speed of 6 kHz to optimize the signal-to-noise ratio, a spectral width of 1 MHz, single pulse excitation for $\tau_p = 1 \mu\text{s}$ ($\gamma B_1/2\pi = 40$ kHz corresponding to $\tau_p^{90} = 6.3 \mu\text{s}$), a repetition delay of 4 s, a line broadening of 10 Hz, and 30000 scans. (b) Simulated spectrum corresponding to the optimized parameters given in Table 1, the experimental conditions given above, a deviation of -0.009° from the exact magic angle, and a probe $Q = 200$. (c) Simulated spectrum corresponding to the parameters in part b except that the probe Q is infinitely low ($Q = 0$) corresponding to ideal excitation/detection. The asterisk in parts a and b indicates the isotropic peak.

As an example the ¹⁴N MAS NMR spectrum of the nitrate ion in KNO₃, recorded at 14.1 T (43.34 MHz) with a spinning speed of 6 kHz and after proper phase/baseline correction, is shown in Figure 1a. The spectrum displays a complete manifold of ssbs, which spans a spectral region of more than 1 MHz and for the most informative part a region of about 700 kHz. Expansions of a few ssbs in two regions away from the center of the spectrum are shown in Figure 2a,c and serve to illustrate the excellent long-term spinning stability (<0.05 Hz) as judged from the extremely well-resolved line shape for the ssbs observed in the outer parts of the spectrum for this and several other nitrates. The appearance of these line shapes depends highly on the angle for the rotor axis (to a precision $\sim 0.001^\circ$) and may serve to determine the deviation of this axis from the exact magic angle of $\theta = 54.736^\circ$ ($3 \cos^2\theta - 1 = 0$). The spectra in Figures 1 and 2 may be compared to those recently obtained by Fung et al.^{2,3} for the nitrate

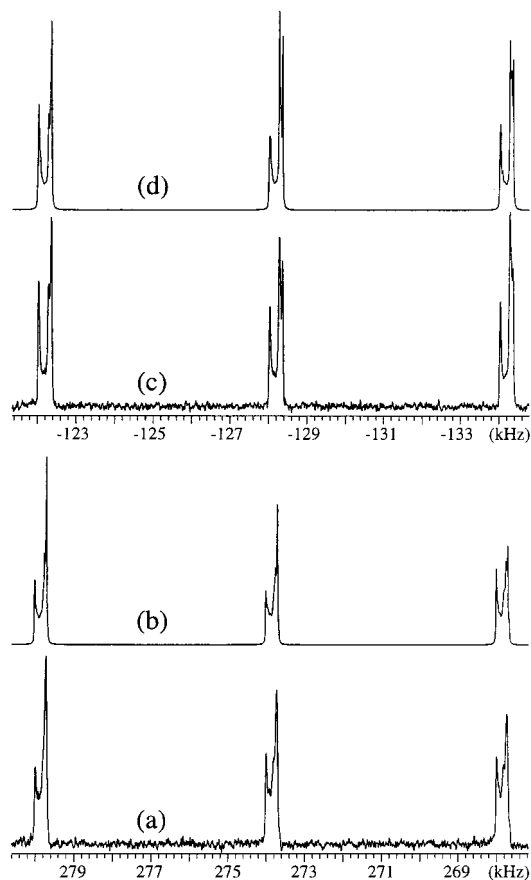


Figure 2. Expansions of spinning sidebands showing the line shape patterns for selected regions in the experimental (a and c) and simulated (b and d) spectra from Figure 1a,b.

ion in KNO_3 , i.e., spectra generally restricted to the observation of a few ssbs and of the spectral features for the centerband (the isotropic resonance) at or near the setting of the magic angle. Since the precise angle settings for these spectra were not determined, values for C_Q and η_Q could not be derived.^{2,3} Although the spectrum in Figure 1a exhibits a dramatic decrease in intensity for the ssbs with increasing order from the centerband, this spectrum and the line shapes of the ssbs in Figure 2 can be analyzed almost to perfection by computer simulations/optimizations in terms of C_Q , η_Q , δ_{iso} , and the experimental conditions using the STARS program.^{4–7} Inclusion of the ^{14}N CSA and most importantly of the second-order cross-term between the quadrupole coupling and CSA (proportional to $v_0\delta_\sigma C_Q/v_0$; a term usually neglected)⁷ in the average Hamiltonian is necessary. Otherwise the line shapes of the ssbs cannot be simulated. The extensive intensity suppression of the ssbs is attributable to the high probe Q (~ 200), commonly employed in ^1H -X MAS probes for sensitivity reasons, at the low ^{14}N resonance frequency. This results in a highly reduced radio frequency bandwidth (50% reduction for a width of $v_0/Q = 43.34/200 = 215$ kHz) during acquisition of the FID compared to the corresponding bandwidth for detection at much higher frequencies (e.g., ^{11}B , ^{23}Na , ^{27}Al) for the same Q value. Taking the probe Q into account along with an optimization of the rotor angle, the optimum simulation for the experimental spectrum (Figure 1a) is shown in Figure 1b. The parameters obtained through the computer optimization are $C_Q = 746 \pm 10$ kHz, $\eta_Q = 0.02 \pm 0.01$, $\delta_{\text{iso}} = 342.7 \pm 0.1$ ppm (relative to solid NH_4Cl), and a deviation of the rotor angle of -0.009° from the exact magic angle. These data are in excellent agreement with the quadrupole coupling parameters determined from single-crystal ^{14}N NMR spectroscopy (see Table 1).¹³ The simulation in Figure 1b includes fixed parameters for the ^{14}N CSA

Table 1. ^{14}N Quadrupole Coupling Parameters (C_Q , η_Q) and Isotropic Chemical Shifts (δ_{iso}) in Nitrate Ions from ^{14}N MAS NMR of Some Inorganic Nitrates

nitrate	C_Q [kHz] ^a	η_Q	δ_{iso} [ppm] ^b
KNO_3	746 ± 10 (751) ¹³	0.02 ± 0.01	342.7 ± 0.1
NaNO_3	740 ± 10 (745) ¹³	0.01 ± 0.01	337.8 ± 0.1
NH_4NO_3^c	620 ± 10	0.25 ± 0.01	335.3 ± 0.1
NH_4NO_3^d	662 ± 10	0.01 ± 0.01	338.9 ± 0.1
$\text{Ba}(\text{NO}_3)_2$	650 ± 10 (651) ¹³	0.01 ± 0.01	340.5 ± 0.1
$\text{Sr}(\text{NO}_3)_2$	614 ± 10	0.01 ± 0.01	338.0 ± 0.1
$\text{Pb}(\text{NO}_3)_2$	539 ± 10	0.00 ± 0.01	334.5 ± 0.1

^a Analysis of the ^{14}N MAS NMR spectra used the values $\delta_\sigma = 145$ ppm and $\eta_\sigma = 0.11$ determined for KNO_3 (see text), the quite similar published values for the two phases of NH_4NO_3 ,¹¹ while for NaNO_3 , $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ we assume the values $\delta_\sigma = 145$ ppm and $\eta_\sigma = 0.00$ for the ^{14}N chemical shift anisotropy. Since the simulations are quite insensitive to the relative orientation of the CSA and quadrupole coupling tensors, in accord with $\eta_Q \approx \eta_\sigma \approx 0$,⁷ we assume coincidence of these tensors. ^b The δ_{iso} values (relative to solid NH_4Cl) include corrections for the second-order quadrupolar shifts which at 14.1 T are in the range of -12 to -22 ppm for the nitrates studied. ^c Data for the NH_4NO_3 phase (IV)¹¹ at about 23 °C. ^d Data for the NH_4NO_3 phase (III)¹¹ at about 35 °C.

($\delta_\sigma = 145$ ppm and $\eta_\sigma = 0.11$), determined as the ^{15}N CSA from ^{15}N MAS spectra of KNO_3 (95% ^{15}N -enriched from Cambridge Isotope Laboratories) at 14.1 T. These data are in good agreement with the values obtained from a single-crystal ^{14}N NMR study of KNO_3 ($\delta_\sigma = 149.8$ ppm and $\eta = 0.010$).¹⁴ Although inclusion of the ^{14}N CSA parameters has a negligible effect on the ssb intensities, it strongly influences the appearance of the line shape for the individual ssbs shown in Figure 2. The significance of considering the high Q for the probe in the analysis of the experimental ^{14}N MAS spectra is clearly illustrated by the simulations in Figure 1. Here the simulation in Figure 1c corresponds to an infinitely low Q (i.e., the probe Q is not taken into account) along with the same, otherwise optimized, parameters used for the simulation in Figure 1b.

In addition to KNO_3 , we have determined C_Q and η_Q parameters from analysis of ^{14}N MAS NMR spectra of similar quality as in Figures 1 and 2 for NaNO_3 , NH_4NO_3 , $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$. These data are summarized in Table 1 and show that the C_Q values vary significantly for these nitrates, while the asymmetry parameters (η_Q) are all close to zero except for NH_4NO_3 at 25 °C. A detailed report on the phase transition for NH_4NO_3 observed by ^{14}N MAS NMR (for NH_4^+ as well as NO_3^-) at ambient temperature will appear elsewhere.

In conclusion, high-quality ^{14}N MAS NMR spectra for nitrogens with ^{14}N quadrupole coupling constants in the range of at least 0.5–1.0 MHz may be acquired using a high- Q MAS probe. Analysis of these spectra using standard programs yields accurate values for the ^{14}N quadrupole coupling parameters C_Q and η_Q , which are useful in the characterization of the local environment for the nitrogen atom. We note that for $C_Q(^{14}\text{N})$ in excess of 1 MHz the wider manifold of ssbs may be mapped by point-by-point acquisition of partial ssb spectra for variable transmitter offsets. The present result opens the door for applications of ^{14}N MAS NMR in many areas of chemistry, e.g., dynamic and binding studies of nitrogen bases, ammonium ions and templates in microporous and mesoporous materials, and studies of phase transitions.

Acknowledgment. The use of the facilities at the Instrument Centre for Solid-State NMR Spectroscopy, University of Aarhus, sponsored by the Danish Natural Science Research Council, the Danish Technical Science Research Council, Teknologistyrelsen, Carlsbergfondet, and Direktør Ib Henriksens Fond, is acknowledged. Financial support from the two Danish Research Councils (J.nr. 5020-00-0018 and J.nr. 0001237) is acknowledged. We thank Dr. Allen G. Palmer, Varian/Chemagnetics for fruitful discussions on the design of the low- γ T3 CP/MAS probe.

JA0100118

(13) Bastow, T.; Stuart, S. N. *Z. Naturforsch.* **1990**, *45a*, 459.

(14) Bastow, T.; Stuart, S. N. *Chem. Phys. Lett.* **1991**, *180*, 305.