High-Resolution ^{14}N Solid-State NMR Spectroscopy**

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The element nitrogen plays an important role in chemistry, particularly in the chemistry of materials and of life. With few exceptions, NMR spectroscopic structure determinations on solid nitrogen compounds have been restricted to the rare spin 1/2 isotope ^{15}N (natural abundance 0.33 %), which usually requires an expensive isotope enrichment. On the other hand it has been assumed since the introduction of high-resolution magic angle spinning (MAS) NMR spectroscopy that the quadrupole interaction precludes the application of this method to ^{14}N, as typical quadrupole couplings are at least two orders of magnitude larger than the sample rotation speeds that were initially achieved. Meanwhile commercial MAS systems have become available that can stabilize spinning speeds between 10 and 20 kHz to about 0.2 ‰. This precision led us to expect that the MAS method would now also be applicable to ^{14}N. In addition to the characterization of the chemical environment of the nitrogen nucleus by the chemical shift and its anisotropy, such experiments would also allow access to the quadrupole interaction and thus to the electric field gradient at the nucleus. Our own interest in this method is focused on its potential for characterizing the nitrogen environment in cubic and hexagonal boron nitride. These compounds in turn are reference compounds for the structure determination of amorphous Si-B-N and Si-B-N-C ceramics.[1]

The application of MAS NMR spectroscopy to ^{14}N measurements on nitrogen nuclei in highly symmetric environments was not expected to pose any problems, as the quadrupole interaction vanishes in tetrahedral or higher symmetry. Indeed, the ^{14}N MAS NMR spectrum of cubic boron nitride was obtained readily with excellent signal-to-noise ratio and high resolution (Figure 1 a). We find a line width of 90 Hz and a chemical shift of $\delta = -17.6$ with respect to NH_4Cl that is also used as a reference in ^{15}N solid-state NMR spectroscopy.[2] The rotational side bands in this spectrum are caused by heteronuclear dipole–dipole couplings with ^{11}B. We were able to exclude a small residual quadrupole interaction arising from slight symmetry deviations by a comparison of ^{10}B and ^{11}B wideline spectra.[3]

To study the influence of a moderate quadrupole interaction on the spectra, we decided to use NH_4SCN as a model sample since it has been well characterized by wideline NMR and by NQR methods.[4] The experimental spectrum assigned to the NH_4^+ ion (quadrupole coupling $\chi = e^2qQ/h = 93$ kHz, $\eta = 1$) is displayed together with a simulation in Figure 2. For the given measurement conditions, no signals are observed that can be attributed to the SCN^- ion ($\chi = 2.28$ MHz). Except for a notable asymmetry in the experimental spectrum, the agreement between experiment and simulation is good; we attribute this asymmetry to a a small anisotropy of the chemical shift. The line width in the MAS spectrum (80 Hz) is reduced by a factor of about 1000 with respect to that in the wideline NMR spectrum. Note that NH_4SCN represents a regime of moderate quadrupole coupling that is also met in some nitrogen-containing phospholipids.[5]

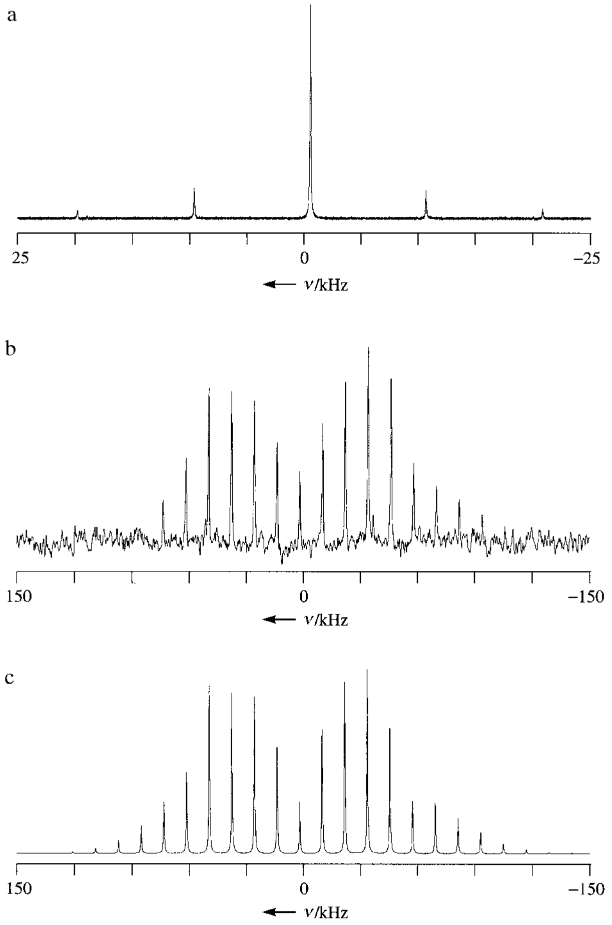

Figure 1. ^{14}N MAS NMR spectra of boron nitrides at 28.809 MHz. a) Cubic boron nitride, $\delta_{iso} = -17.6$ ppm; b) hexagonal boron nitride; c) simulation of the spectrum of hexagonal boron nitride with the parameters $\delta_{iso} = 63$ ppm, $\Delta\sigma = 160$ ppm, $e^2qQ/h = 140$ kHz, $\eta = 0$.

Encouraged by the relatively high sensitivity of ^{14}N MAS NMR spectroscopy for moderate quadrupole couplings, we applied the method to hexagonal boron nitride. In this case we were not able to obtain a ^{14}N wideline NMR spectrum under static conditions. As a result of the rigid lattice and of the absence of protons, spin-lattice relaxation of ^{14}N is quite slow, so that the optimum recovery time between the measurement of two transients is as long as 30 minutes. Nevertheless, a spectrum with satisfactory signal-to-noise ratio can still be obtained (Figure 1 b). For the simulation of this spectrum, we have extended the method by Herzfeld and Berger to the case of a spin 1 with quadrupole coupling and anisotropic chemical shift.[6] By fitting the parameters and subsequently correcting the isotropic shift by the second-order quadrupole contribution, we otain the values $\chi = 140 \pm 10$ kHz, $\delta_{iso} = 63 \pm 3$ ppm, and an anisotropy of the chemical shielding of $\Delta\sigma = 160 \pm$

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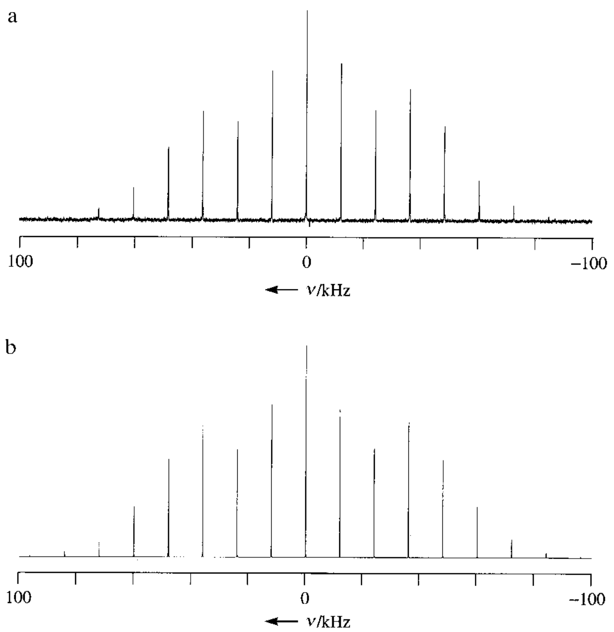

Figure 2. ^{14}N MAS NMR spectrum of ammonium thiocyanate at 28.809 MHz. a) Experimental spectrum; b) simulation with quadrupole coupling parameters taken from literature.[4]

20 ppm. Hereby, on the basis of the known crystal structure we have assumed axial symmetry of both tensors ($\eta = 0$). Evidently, three-coordinate nitrogen in hexagonal boron nitride can be safely distinguished from four-coordinate nitrogen in cubic boron nitride solely based on the isotropic chemical shift. The chemical shift found for the hexagonal modification is in relatively good agreement with a calculated value ($\delta = 56 \pm 5$ ppm with respect to NH_4Cl),[7] while χ is unexpectedly low. Note, however, that the strong dependence of the theoretical results for χ (0.75 – 1.33 MHz)[8] on the basis set already reveals some difficulties in these calculations. Furthermore, it is remarkable that the anisotropy of the chemical shift can be estimated from the side band pattern, although it is smaller than the sample rotation speed.

From the spectra in Figures 1 and 2 one may conclude that ^{14}N MAS NMR spectroscopy with contemporary spectrometers should also be feasible for larger χ values of about 1 MHz. Indeed we have also succeeded in detecting MAS side band patterns for glycine ($\chi = 1.25$ MHz[9]). However, to be able to analyze spectra in this regime of medium quadrupole couplings quantitatively, further developments are needed mainly in broad band spectral excitation. In this respect it is also significant that state-of-the-art commercial spectrometers now achieve 50 % larger resonance frequencies and three times faster sample spinning than are used in this work. These developments should drastically improve the performance of ^{14}N MAS NMR spectroscopy for larger quadrupole couplings. With such experiments, an important gap in the applicability of high-resolution NMR spectroscopy is finally closed.

Experimental Section

All NMR spectra were measured with a Unity 400 NMR spectrometer (Varian) and a 5-mm MAS probe head (Doty) at a resonance frequency of $\nu_0 = 28.809$ MHz and a sample rotation speed of 12 kHz. The length of a 90° pulse was 6 μs, to obtain more uniform excitation over a broader band and to improve sensitivity we have measured all spectra with excitation pulses of 2 μs duration. Cubic boron nitride (MICRONABN300, DeBeers), hexagonal boron nitride (99 %, Aldrich), NH_4SCN, NH_4Cl, and glycine (Merck) were used without further purification. Spectra were simulated with the program WIN-MAS (Bruker). The anisotropy tensors for the two NMR transitions of a spin-1 nucleus are calculated from the shielding tensor $\boldsymbol{\sigma}$ and the quadrupole tensor $\boldsymbol{\chi}$ as $\boldsymbol{\sigma} \pm 3\boldsymbol{\chi}/(4\nu_0)$. The spectra of the two transitions were calculated separately and added. For NH_4SCN we have neglected $\boldsymbol{\sigma}$. Second-order contributions of the quadrupole coupling were neglected in the simulation of the side band patterns in both cases.

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Methyl Transfer from Methanol to Co – cobyrinate: A model for the Coenzyme B_{12} Dependent Methyltransferase?**

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Methanol can be used by certain methanogenic and acetogenic microorganisms as a source of methyl in the synthesis of methane and acetyl-CoA.[1–4] In the cases reported, Co – corrinoids function as prosthetic groups and form $Co-CH_3$ complexes, which transfer the methyl group to coenzyme M ($HSCH_2CH_2SO_3^-$) or possibly to tetrahydro-

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