Inorg. Chem. **2006**, *45*, 437–442

New Signal Processing Method for the Faster Observation of Natural-Abundance ^{15}N NMR Spectra and Its Application to N_5^+

Sharif D. Kunikeev, Howard S. Taylor,* Thorsten Schroer,* Ralf Haiges, C. J. Bigler Jones, and Karl O. Christe*

Department of Chemistry and Loker Research Institute, University of Southern California, Los Angeles, California 90089

Received October 3, 2005

The new harmonic inversion noise reduction method was applied to ^{15}N natural-abundance NMR spectroscopy and N_5SbF_6. This method is superior to conventional Fourier transform methods for processing FIDs and permits the detection of natural abundance ^{15}N NMR signals with significantly reduced numbers of scans and improved sensitivity. In addition to the confirmation of the previously reported chemical shifts for N_5^+, the one bond coupling between N_β and N_γ could be observed for the first time. Its absolute value is compared to known coupling constants of other covalent azides and the free azide ion.

Introduction

The successful synthesis[1] of N_5AsF_6 in 1999 has stimulated worldwide interest in the preparation of new homonuclear polynitrogen species. The synthesis of such highly endothermic compounds[2] presents an enormous challenge to the preparative chemist. In addition, the positive identification of these compounds is very difficult. In theory, nitrogen NMR spectroscopy appears to be ideally suited for this purpose. In practice, however, nitrogen NMR spectroscopy presents significant problems. Whereas the ^{14}N nucleus has a high natural abundance of 99.63% (receptivity compared to ^{13}C: $R_C = 5.7$),[3] it possesses a spin of $I = 1$, resulting in quadrupolar relaxation and line broadening. Therefore, the ^{14}N resonances are only observable for nitrogen in a highly symmetric electronic environment.

The second naturally occurring nitrogen isotope, ^{15}N, possesses a nuclear spin of $I = {}^1/_2$. However, its natural abundance of 0.37% ($R_C = 2.19\times10^{-2}$) [3] is very low. In addition, relaxation times of the ^{15}N nucleus are quite long (up to 450 s), which necessitates long delay times between scans. Therefore, high sample concentrations and "unlimited" instrument time are usually required to record ^{15}N NMR spectra in natural abundance. Although the addition of relaxation reagents, such as $Cr(acac)_3$, and ^{15}N enrichment might be used to overcome some of these complications, compatibility problems of strong oxidizers, such as N_5^+, with $Cr(acac)_3$ and difficult syntheses, as for polynitrogen compounds or complex proteins, can mitigate such approaches.

Recently, a new signal processing method,[4] harmonic inversion noise reduction (HINR), was proposed for the detection of weak NMR signals which are unobservable by conventional Fourier transform (FT) techniques. This method was already successfully employed for the detection of $^{13}C-^{13}C$ couplings,[4] the observation of ^{13}C satellites in ^{31}P NMR spectra, and the recording of ^{17}O NMR shifts without enrichment.[5]

In this paper, we demonstrate the potential of the HINR method for nitrogen NMR spectroscopy by measurement of the natural abundance ^{15}N NMR spectrum of N_5SbF_6 in anhydrous HF (aHF) solution. The chemical shifts of the three nonequivalent nitrogen atoms of N_5^+ had previously been reported,[1] but the S/N ratio was poor and the $^1J_{N,N}$ couplings were not observed.

Experimental Section

Caution! *HN_3, azides and polynitrogen compounds are highly endothermic and can decompose explosively. They should be handled only on a small scale with appropriate safety precautions*

* To whom correspondence should be addressed. E-mail: taylor@usc.edu (H.S.T.); kchriste@usc.edu (K.O.C.); schroer@usc.edu (T.S.).

(1) Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2004.
(2) Dixon, D. A.; Feller, D.; Christe, K. O.; Wilson, W. W.; Vij, V.; Vij, A.; Jenkins, H. D. B.; Olson, R. M.; Gordon, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 834.
(3) Mason, J., Ed. *Multinuclear NMR*; Plenum Press: New York, 1987; p 335 ff.
(4) Kunikeev, S. D.; Taylor, H. S. *J. Phys. Chem. A* **2004**, *108*, 743.
(5) Kunikeev, S. D.; Taylor, H. S.; Pan, J.-J.; Kershaw, A.; McKenna, C. E. *J. Organomet. Chem.* **2005**, *690*, 2644.

10.1021/ic051705a CCC: $33.50
Published on Web 11/22/2005

(face shields, leather gloves and protective clothing). Condensation of neat HN_3 at −196 °C into Teflon ampules containing oxidizers must be avoided. It should always be co-condensed with an appropriate solvent to minimize the risk of explosion upon condensation or melting of HN_3.

Using literature methods, N_5SbF_6 and singly ^{15}N-labeled $N_5{}^*SbF_6$ were prepared from N_2FSbF_6 [6] and HN_3. HN_3 was prepared from NaN_3 (Aldrich) or $NaN_3{}^*$ which was labeled at one terminal nitrogen (Cambridge Isotopes), respectively, using a large excess of HF.[7] HF was dried[8] over BiF_5 (Ozark Mahoning) and stored over K_2NiF_6 (Ozark Mahoning) prior to its use.

In the dry atmosphere of an argon glovebox, N_5SbF_6 (0.0948 mmol) and $N_5{}^*SbF_6$ (0.1350 mmol), respectively, were loaded into 3 mm o.d. Teflon-FEP tubes, which were heat-sealed at one end and closed by a Hoke stainless steel valve at the other. The reactors were connected to a stainless steel vacuum line, and aHF (522 and 325 mg, respectively) was condensed on top of the solids at −196 °C. The samples were briefly warmed to −20 °C to dissolve the salts. The solutions were frozen at −196 °C, and the Teflon-FEP ampules were heat-sealed under vacuum and stored in a freezer at −20 °C until the spectra could be recorded (concentrations of the aHF solutions: $N_5SbF_6 = 0.19$ mol/L; $N_5{}^*SbF_6 = 0.44$ mol/L).

The ^{14}N and ^{15}N NMR spectra were recorded on a Bruker AMX-500 NMR instrument at 36.13 and 50.68 MHz, respectively, using a 5 mm broad band probe. All spectra were collected at −20 °C to avoid the decomposition of N_5SbF_6 in aHF. Neat CH_3NO_2 ($\delta = 0$ ppm), measured at room temperature, was used as an external standard. In the case of ^{14}N, a pulse angle corresponding to a pulse width of 8 μs and a spectral width of 18518.5 Hz were used. The acquisition time was 1.77 s, and the delay between scans was 0.5 s. The ^{15}N NMR spectra were recorded using a pulse angle corresponding to a pulse width of 6 μs.

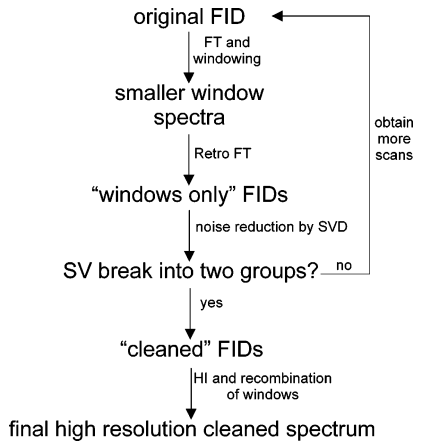
The unlabeled N_5SbF_6 sample was measured using a spectral width of 20833.3 Hz. The acquisition time was 3.15 s, and the delay between scans was 3 s, resulting in a total time of 6.15 s per scan. Twenty nine data blocks, each consisting of 400 scans, were recorded. Afterward, the blocks were sequentially added up until a satisfying S/N ratio was obtained using FT or HINR processing, respectively.

For the singly ^{15}N-labeled $N_5{}^*SbF_6$ sample, a spectral width of 26315.8 Hz, an acquisition time of 2.49 s, and a delay between scans of 1 s for a total of 3.49 s per scan were used. Nine FIDs, each consisting of 4000 scans, were recorded. The data were processed as in the case of unlabeled N_5SbF_6.

Description of the HINR Method. The HINR method (for its mathematical description, see ref 4) is an alternative to the conventional FT approaches used for converting a time-dependent FID into a frequency domain spectrum. Its principle is depicted in Scheme 1.

To avoid large matrixes and/or large numbers of coupled linear equations which can lead to numerically unstable results, a windowing technique is employed.[9] In the first step, the original FID is Fourier transformed, and the resulting spectrum is then segmented into smaller windows, each consisting of about 300 Fourier grid points. Working window by window, the frequency spectrum outside the window of interest is discarded and Fourier transformed back to the time domain inside the window of interest (step 2). The resulting new FID contains fewer entries, as it corresponds to a much smaller bandwidth. For example, if the particular window bandwidth is one-fifth of the original bandwidth, then only every fifth sample point is needed in the new FID. This decimated FID provides the new input for the HINR method. As Fourier periodicity has been violated, the spectral product of the procedures below cannot be trusted at the window edges, and overlapping windows must be taken if the region of interest is not restricted to the interior of the window.

Scheme 1. Principal of the HINR Method



In the next step, the signal is processed in time space to achieve a noise reduced (NR) "cleaned" FID. The use of singular value decomposition (SVD) to create a "cleaned" signal may be unfamiliar to chemists but is pervasive in signal processing theory. FIDs are assumed to be sums of true and random noise signals. Using the sample data available in the FID, a Hermitian correlation matrix is created and subjected to the SVD process, which here just corresponds to diagonalizing the correlation matrix.[4] The resulting all-positive singular values of this matrix are arranged in decreasing order. When the number of scans is sufficient, so that the singular values divide themselves into a recognizable higher-valued and lower-valued group, the experiment is stopped. The lower SV group is then discarded as it is associated with most of the noise. A procedure[9] involving the windowed FID and the retained singular values and singular vectors, is used to create a "cleaned" signal. Hindsight tells us that the gap usually appears when the S/N ratio for the peak of interest is roughly 1.1. At this ratio, the conventional FT spectrum of the raw FID does not allow positive identification of the given signals due to excessive noise, even with use of matched filters. On the other hand, the FT spectrum of the "cleaned" FID does show the desired spectrum.

A higher-resolution and better-defined spectrum can be achieved from this signal by harmonic inversion (HI).[10,11] The HI method (step 4) is less generic than Fourier analyses. It gives acceptable results only when the cleaned FID is used. Furthermore, it assumes that the spectrum will be composed of Lorentzians, corresponding to a FID signal which is modeled by a weighted sum of damped harmonics (complex exponentials). This limits the method to solution-phase NMR. In a minimal error sense, the method fits the Lorentzian parameters which appear in the complex exponentials to the "cleaned" FID data. As such, the advantages of the HI over

(6) Christe, K. O.; Wilson, R. D.; Sawodny, W. *J. Mol. Struct.* **1971**, *8*, 245. Christe, K. O.; Wilson, R. D.; Wilson, W. W.; Bau, R.; Sukumar, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 1991.
(7) Vij, A.; Wilson, W. W.; Vij, V.; Tham, F. S.; Sheehy, J. A.; Christe, K. O. *J. Am. Chem. Soc.* **2001**, *123*, 6308.
(8) Christe, K. O.; Wilson, W. W.; Schack, C. J. *J. Fluorine Chem.* **1978**, *11*, 71.
(9) Cadzow, J. A. *IEEE Trans. Acoust., Speech, Signal Process.* **1988**, *36*, 49.
(10) Main, J.; Dando, P. A.; Belkic, D.; Taylor, H. S. *J. Phys. Chem. A* **2000**, *104*, 1247.
(11) Belkic, D.; Dando, P. A.; Main, J.; Taylor, H. S.; Shim, S. K. *J. Phys. Chem. A* **2000**, *104*, 11677.

the FT method are (a) it achieves a higher-resolution spectrum and (b) it produces the Lorentzian parameters (frequency, area, and width) simultaneously with the spectrum. Clearly, the HINR method can detect spectral features that normally would require many more scans with the standard FT approach. Experience indicates that reductions in the number of needed scans range from 2- to 60-fold. As a consequence, the new method can be used either to conserve spectrometer time or to reveal spectral features when signals are too weak to be detected conventionally.

The improvement of the sensitivity of the spectrum using a matched filter is not possible. The measured FID and the resulting FT spectrum, which is available when the SVs first divide, is too noisy. Therefore, the noise in the spectrum and in the FID does not allow the observation of a signal width in the former or a decay rate in the latter. However, these inputs are required to use matched filters.

In the case of the HINR method, frequencies converge fastest and areas soon follow, but line widths which are of instrument origin are less accurately obtained. Since line heights are area divided by width, an error in the line width can make the Lorentzian line appear too intense and too narrow, even though the sought-after frequency and area are correct. The noiselessness and occasional peak narrowness might be surprising to an observer who is accustomed to FT spectra.

In contrast to FT spectra, the error due to remaining noise is in the Lorentzian parameter values and in resolution power. Imagine a doublet signal exhibiting a small coupling constant with an absolute J value that is just in the range of the digital resolution of the collected data. In the case of the FT method, a signal consisting of two more or less overlapping lines is seen if the S/N ratio is high enough. At low S/N ratio, the FT method first sees only noise and then, with increasing number of scans, a poorly resolved signal with superimposed noise encompassing the area of the two peaks.

In the above-mentioned case, the HINR method behaves in a slightly different way. Theoretical arguments[12] show that at first a gap between one high and many low SVs will appear When the noise-reduced FID is treated by using the HI method, a single broad peak, albeit without the superimposed noise, will appear. Increasing the number of scans, the highest noisy SV will rise somewhat above the "true" noise SVs at σ^2 and reveal a new SV grouping with two SVs separated in value from the noise SVs. Using the new noise-reduced FID, the HI method will produce a signal consisting of two overlapping peaks as would be achieved by the FT method with a high S/N ratio FID. This phenomenon not only occurs in near-degenerate cases but also when there are for example two nonoverlapping signals of totally different intensities. The key point of course is that the HINR method will see the results with much fewer scans. The method will show the single peak when the FT method only sees noise and will see the doublet peak soon after.

In summary, once a stable gap appears in the singular values, the new method produces a spectrum which has a higher sensitivity than the spectrum obtained by using conventionally Fourier methods with the same number of scans. Previous methods using the SVD procedure have either missed true lines or seen false ones due to their failure to keep scanning until a stable gap was reached.

Results and Discussion

The V-shaped N_5^+ cation (C_{2v} symmetry) possesses three chemically different nitrogen atoms (Figure 1).[7] Therefore, the ^{15}N NMR spectrum of N_5SbF_6 exhibits three signals for

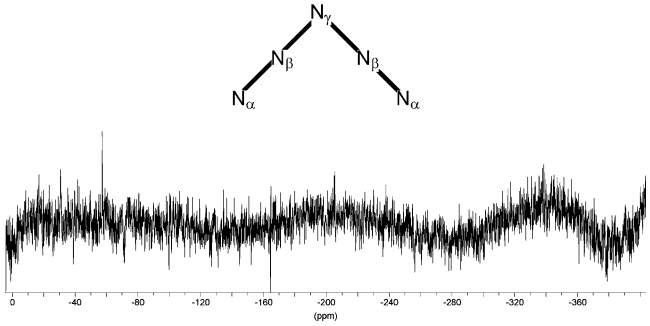


Figure 1. Natural-abundance ^{15}N NMR spectrum of N_5SbF_6 in aHF (c = 0.19 mol/L) at −20 °C after 11 600 scans.

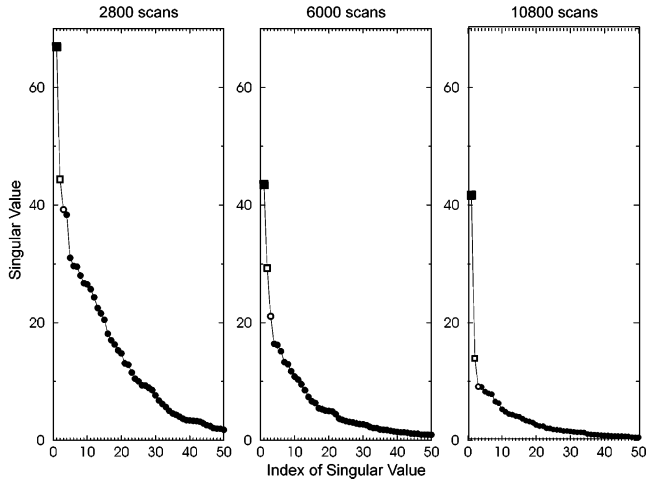


Figure 2. Distribution of the singular values after different number of scans for the −145 to −185 ppm window.

N_α, N_β, and N_γ with an area ratio of 2:2:1. Figure 1 shows the conventional ^{15}N spectrum of unlabeled N_5SbF_6 in aHF (c = 0.19 mol/L) at −20 °C after processing the FID of 11 600 scans with the common FT method using a line-broadening of 5 Hz. As can be seen, the concentration of ^{15}N is too low to assign any signal with confidence.

Spectrum of Unlabeled N_5SbF_6. The same raw data were then processed using the HINR method. The nitrogen NMR shifts for N_α (−100.4 ppm), N_γ (−237.3 ppm), and N_β (−165.3 ppm) were known from previous ^{15}N-labeling experiments and from ^{14}N NMR measurements, respectively.[1] Therefore, only three windows from −80 to −120, −145 to −185, and −220 to −260 ppm were processed to demonstrate the method. When the chemical shifts are unknown, the whole spectrum must be windowed and processed. Windows without signals can be recognized as they show no stable gap and have SVs that drop in value as the inverse of the square of the number of scans.

Figure 2 demonstrates the noise-reduction process for the window containing the N_β signal. After 2800 scans, there were four singular values equal or larger than approximately 40 (black and white square, white and first black circle). The next 11 values were between 31 and 20, while the remaining ones were below 20. After 6000 scans, the distribution of singular values changed dramatically. With exception of the first three, all of the values were now well below 20. The biggest gaps were between the first four

(12) Kunikeev, S. D.; Taylor, H. S., to be published.

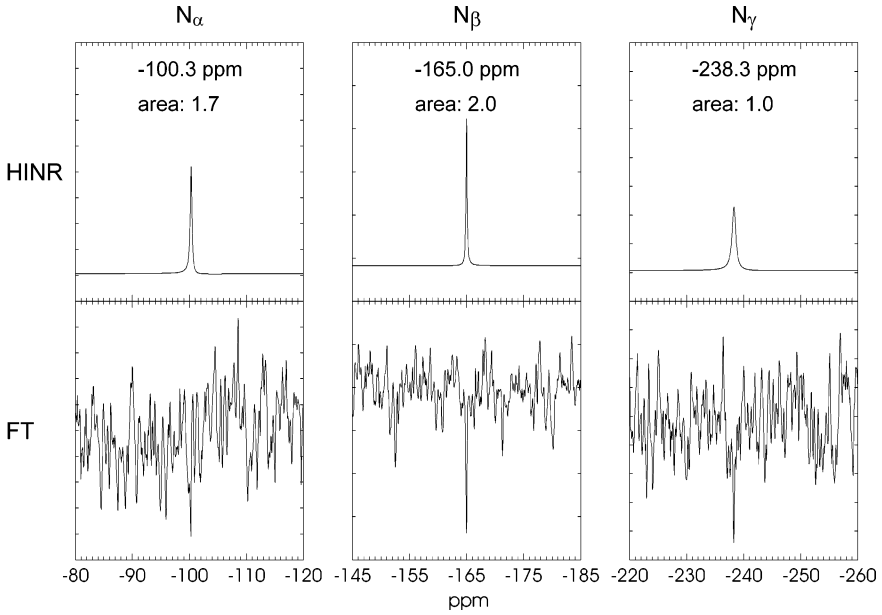


Figure 3. Comparison of the natural-abundance ^{15}N NMR spectra of N_5SbF_6 in aHF (c = 0.19 mol/L) at −20 °C using the HINR and the conventional FT methods.

singular values. After 10 800 scans, a stable, well-defined gap was reached between the first and the second SV. All singular values, with exception of the first one, dropped below 20, and only the first singular value stayed stationary. Therefore, the sought gap had to be between the first and the second singular values.

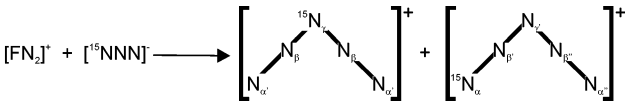
The singular values above the gap are used to project the noise out of the measured signal and to create a noise-reduced FID. One must keep in mind that there is neither a linear relationship between the SVs and the frequency and area of the signal nor is the number of values above the gap necessarily equal to the number of signals in the window. However, the number of signals in the window cannot be greater than the number of singular values above the gap.

Applying the harmonic inversion (HI) method to the "cleaned" FIDs of all three windows, the three ^{15}N NMR signals of the N_5^+ cation were found after 10 800 scans (Figure 3). The resulting chemical shifts (N_α = −100.3, N_β = −156.0, and N_γ = −238.3 ppm) are in excellent agreement with the previously observed shifts.[1] The ratio of $N_\alpha/N_\beta/N_\gamma$ was 1.7:2:1. The lower value for N_α was probably caused by a relaxation effect. The delay between scans was set to 3 s in order to get a higher number of scans during the available measuring time. As the spin−lattice relaxation time for ^{15}N can be up to 450 s,[3] the relaxation process was probably not completed before the next acquisition was started. If the spin−lattice relaxation time for N_α is longer than those for N_β and N_γ, a lower-than-expected area value results for N_α.

Figure 3 is an impressive example for the potential of the HINR method. While after 11 600 scans the conventional FT method (lower traces which are blow ups of Figure 1) could not produce clear evidence for the signals, the HINR method, using even less scans, successfully provided all signals.

Spectrum of ^{15}N-Labeled N_5SbF_6. The natural abundance of ^{15}N (0.37%) is very low. Therefore, the probability that two ^{15}N nitrogen atoms are connected to each other is only 1.37×10^{-5}. For a saturated solution of unlabeled N_5SbF_6 in aHF at −20 °C ($c \approx 0.4$ mol/L), the concentration of N_5^+ cations with two neighboring ^{15}N atoms is only 5.48×10^{-6} mol/L. This concentration is much too low to allow the observation of $^1J_{^{15}N,^{15}N}$ couplings. However, ^{15}N labeling of the N_5^+ cation in one position improves these odds sufficiently to permit the observation of these couplings by the HINR method.

Using the singly ^{15}N-labeled azide ion in the synthesis of N_5SbF_6, two different singly ^{15}N-labeled isotopomers of N_5^+ are formed.



Half of the N_5^+ cations carry the ^{15}N label in the N_γ position, while in the other half, one of the two N_α atoms is ^{15}N labeled. The probabilities of neighboring ^{15}N atoms for the N_β−N_γ and $N_{\beta'}$−N_α pairs increase to 0.37% and 0.185%, respectively. Therefore, in a saturated solution of N_5SbF_6 in aHF at −20 °C, the concentrations of N_5^+ ions containing either $^{15}N_\beta$−$^{15}N_\gamma$ or $^{15}N_\alpha$−$^{15}N_{\beta'}$ moieties are 1.48×10^{-3} and 7.4×10^{-4} mol/L, respectively.

$^1J_{^{15}N,^{15}N}$ couplings are rather small. They usually are negative and lie between −5 and −25 Hz.[13] The spectra obtained after 32 000 scans, using the conventional FT and the HINR method for processing the FID, are shown in Figure 4.

In the region of the N_α atom, only a singlet was observed at −99.7 ppm. The absolute value of the coupling constant $^1J_{^{15}N-^{14}N}$ between $^{15}N_\alpha$ and $^{14}N_{\beta'}$ appears to be too small to resolve the expected 1:1:1 triplet. This is in accordance with

(13) Berger, S.; Braun, S.; Kalinowsky, H.-O. *NMR Spectroscopy of the Non-Metallic Elements*; John Wiley and Sons: New York, 1997; p 271 ff.

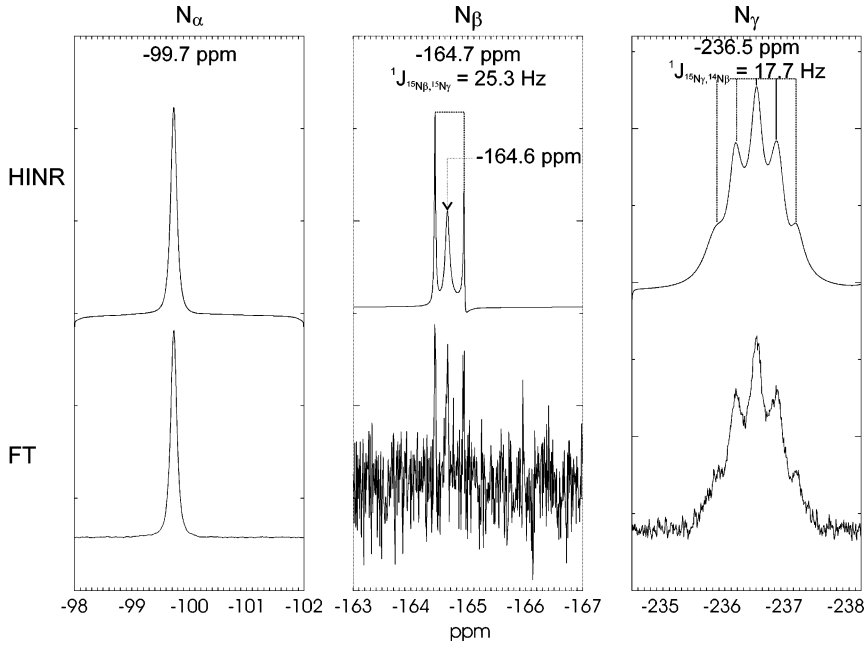


Figure 4. Comparison of the ^{15}N NMR spectra of ^{15}N-labeled N_5SbF_6 in aHF (c = 0.44 mol/L) at −20 °C using the HINR and the conventional FT methods.

the common observation[14] that coupling constants involving terminal nitrogen atoms are very small. The much weaker signals for the natural abundance $N_{\alpha'}$ and $N_{\alpha''}$ nitrogen atoms are obscured by this strong singlet.

In the absence of quadrupolar relaxation effects and with the knowledge that the coupling constant between N_α and N_β is too small to be resolved, the $^{15}N_\beta$ signal at −165 ppm should be composed of three signals with very similar chemical shifts: (i) a doublet ($^1J_{^{15}N_\beta,^{15}N_\gamma}$) for N_β; (ii) a 1:1:1 triplet ($^1J_{^{15}N_{\beta'},^{14}N_{\gamma'}}$) for $N_{\beta'}$; and (iii) a 1:1:1 triplet ($^1J_{^{15}N_{\beta''},^{14}N_{\gamma'}}$) for $N_{\beta''}$, with area ratios of 2:1:1, respectively. Although the standard FT method indicates the presence of a signal at about −165 ppm, the S/N ratio is very poor and it is not clear how many lines are in this region. This ambiguity was resolved by the HINR method.

Clearly, there are only three signals present. The deviations from the predicted complicated spectrum are caused by the asymmetric electronic environment around the quadrupolar $^{14}N_{\gamma'}$ (I = 1) nucleus, causing the $^{15}N_\beta$−$^{14}N_\gamma$ splitting to collapse into a single line at −164.64 ppm. Therefore, the left signal at −164.43 ppm and the right one at −164.93 ppm belong to N_β, split into a doublet by $^{15}N_\gamma$ with $^1J_{^{15}N_\beta,^{15}N_\gamma}$ = 25.3 Hz. After correction by the ratio of the gyromagnetic constants[3] of ^{14}N and ^{15}N,

$$J_{^{14}N,^{15}N} = J_{^{15}N,^{15}N}/1.403 = 25.3/1.403 = 18.0 \text{ Hz}$$

its absolute J value is in accord with that of $^1J_{^{15}N_\gamma,^{14}N_\beta}$ = 17.7 Hz, found in the quintet of the $^{15}N_\gamma$ signal at −236.5 ppm of Figure 4. On the basis of the observed area ratios, the signals for $N_{\beta'}$ and $N_{\beta''}$ coincide in the central, broader signal at −164.64 ppm. These assignments are further supported by the similar pattern observed for the different N_β atoms in the ^{14}N NMR spectrum (see below).

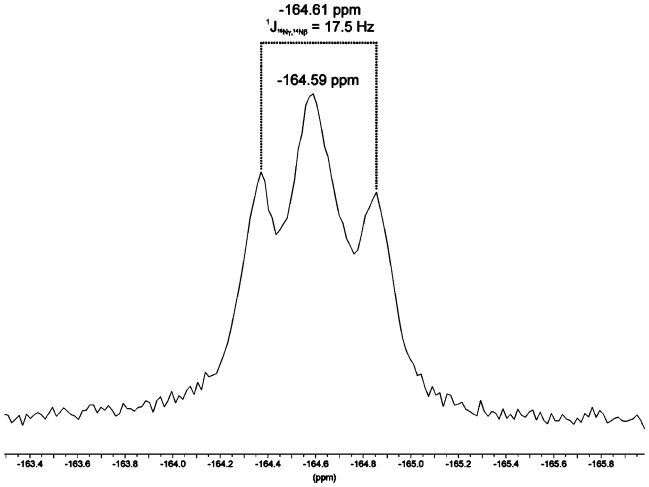


Figure 5. ^{14}N NMR signal of N_β of ^{15}N-labeled N_5SbF_6 in aHF (c = 0.44 mol/L) at −20 °C.

In the region of N_γ, a quintet is observed in the ^{15}N NMR spectrum (Figure 4). This splitting is due to the coupling with two adjacent $^{14}N_\beta$ nitrogen atoms with I = 1, giving rise to a 1:2:3:2:1 quintet with an absolute coupling constant of $^1J_{^{15}N_\gamma,^{14}N_\beta}$ = 17.7 Hz. The same coupling (17.5 Hz) was observed in the ^{14}N NMR spectrum of this sample for the $^{14}N_\beta$ nitrogen signal at −164.59 ppm (Figure 5).

The pattern and analysis of this signal are analogous to those discussed above for the $^{15}N_\beta$ signal of Figure 4. It appears to be a triplet but actually is a superposition of a doublet for $^{14}N_\beta$ ($^1J_{^{15}N,^{14}N}$ = 17.5 Hz) and coinciding singlets for $^{14}N_{\beta'}$ and $^{14}N_{\beta''}$, which form the center of the signal.

(14) Mason, J. Nitrogen NMR. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K, Eds.; John Wiley and Sons: New York, 2002.
(15) Schatte, G.; Willner, H.; Willert-Porada, M. *Magn. Reson. Chem.* **1992**, *30*, 118.
(16) Müller, J. *Z. Naturforsch.* **1978**, *B33*, 993.
(17) Müller, J. *Z. Naturforsch.* **1979**, *B34*, 437.
(18) Müller, J. *J. Organomet. Chem.* **1973**, *51*, 119.

Table 1. $^1J_{^{15}N,^{15}N}$ between the Substituted Nitrogen and the Central Nitrogen of Covalent Azides and the Free Azide Ion

	solvent	$^1J_{^{15}N,^{15}N}$/Hz	ref
FN_3	CD_2Cl_2	26.5	15
$N_2^+N_3$	HF	25.3	
ClN_3	CD_2Cl_2	24.0	16
CH_3N_3	C_6F_6	14.4	17
HN_3	Et_2O	14.0	16
N_3^-	D_2O	11.3	18

It should be noted that the $^1J_{^{15}N_\gamma,^{14}N_\beta}$ quintet is observed in the N_γ region, but neither the $^1J_{^{15}N_{\beta'},^{14}N_\gamma}$ nor the $^1J_{^{15}N_{\beta''},^{14}N_\gamma}$ triplet is seen in the N_β region of the ^{15}N NMR spectrum. Obviously, if the quadrupolar ^{14}N nucleus is in an electronic field of low symmetry, only the splitting of the ^{14}N signal due to ^{15}N but not the splitting of the ^{15}N signal due to ^{14}N is observable.

In the $^{15}N_\gamma$ signal of the natural-abundance sample (Figure 3), the quintet fine structure, seen in the corresponding signal of the enriched sample (Figure 4), was not observed. As can be seen from the S/N ratios in the FT spectra of Figures 3 and 4, the quality of the raw data for the natural abundance spectrum is much worse than for the enriched sample because of the lower ^{15}N concentration. Therefore, the S/N ratio of the raw data of the unlabeled N_5SbF_6 sample is only sufficient to see the envelope of the quintet in the noise-reduced HINR spectrum. As explained previously, the S/N ratio is between the levels, which allows the location of the desired signal but is insufficient for the observation of the fine structure using the HINR method.

The absolute value of $^1J_{^{15}N_\beta,^{15}N_\gamma} = 25.3$ Hz is one of the largest $^1J_{^{15}N,^{15}N}$ values observed to date. Only fluorine azide (or triazadienyl fluoride), FN_3, exhibits a larger $^1J_{^{15}N,^{15}N}$ coupling constant of 26.5 Hz.[13] Little is known about the relationship between $^1J_{^{15}N,^{15}N}$ and the properties of the molecule, although in covalent azides, the absolute value of $^1J_{^{15}N,^{15}N}$ seems to increase with increasing electronegativity of the ligand (Table 1).

Conclusion

The new HINR method is superior to conventional Fourier transform methods for processing FIDs of ^{15}N NMR spectra. It permits the detection of natural-abundance ^{15}N NMR signals with significantly reduced numbers of scans and greatly improved sensitivity. It is a powerful tool for the identification of polynitrogen compounds using ^{15}N NMR spectroscopy and could hold great potential for other nitrogen-containing compounds, such as proteins, where ^{15}N enrichment is synthetically very difficult or the nitrogen concentrations are so low that prohibitively long data collection times are required. This method might also be used to study NMR spectra of other nuclei of low natural abundance which have a low receptivity and long relaxation times, (for example ^{33}S, ^{183}W, ^{187}Os, etc.). Therefore, the HINR method could be very beneficial not only for energetic polynitrogen compounds but also for bioinorganic chemistry, catalysis research, and similar fields.

The routine use of this method in general NMR laboratories will require the development of suitable software packages. This step is beyond our present capabilities and financial resources. It is hoped that either the leading NMR instrument manufacturers or some independent software development companies will write the required programs and incorporate them into their routine packages, thereby making this powerful new tool available to the general scientific community.

Acknowledgment. The authors thank Allen Kershaw for his invaluable advice and help with the data collection. This work was financially supported by the National Science Foundation (Grant Nos. CHE-0330677 and CHE-0456343), the Air Force Office of Scientific Research, and the Office of Naval Research.

IC051705A