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Protonation Nitrogen Shielding and NOE in Aqueous Nitrite and Solid-State ^{15}N NMR of $NOBF_4$ and NO_2BF_4

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Nitrogen-15 chemical shift measurements carried out under NO at 1 atm and pH ≥ 2.2 yield the value $\Delta(\delta^{15}N) = -30.4$ ppm for the total protonation shielding of $NO_2^-(aq)$. Measurements at higher acidity levels reflect the increasing significance of NO^+ and confirm the presence of two ^{15}N resonances, one sharp and one broadened, in the region around 45% D_2SO_4. Assignment of the sharp peak to NO^+ is confirmed by solid-state NMR of $NOBF_4$. Broadening in the other suggests that exchange between HNO_2 and some form of acidium ion (e.g. $H_2NO_2^+$) precedes NO^+ release, but no NOE is detected in 42.4% D_2SO_4 and it is inferred that no proton-to-nitrogen connnectivity occurs in this species. Nitrogen-15 chemical shifts and chemical shift anisotropies have been obtained in the solid state at natural isotopic abundance for the nitrosonium and nitronium ions in their respective tetrafluoroboride salts.

At low acidity in the absence of added nucleophiles, nitrosation by nitrous acid[1] is second order in HONO, reflecting a reactive agent generally agreed to be dinitrogen trioxide (eq 1). Acid-

$$2HNO_2(aq) \rightleftarrows N_2O_3(aq) + H_2O \qquad (1)$$

catalyzed nitrosation, on the other hand, first order both in HNO_2 and in H^+, was interpreted initially in terms of an assumed "nitrous acidium ion" $H_2NO_2^+$ (eq 2), although it could also occur via

$$HNO_2(aq) + H_3O^+(aq) \rightleftarrows H_2NO_2^+(aq) + H_2O \qquad (2)$$

attack of the nitrosonium ion NO^+, formed either via a distinct hydrate or in a direct process (eq 3). There is abundant

$$H_3O^+(aq) + HNO_2(aq) \rightleftarrows NO^+(aq) + 2H_2O \qquad (3)$$

spectroscopic evidence for the presence and reactivity of NO^+ in nitrite solutions at high acidity,[2] but the presence or absence and reactive significance of the species $H_2NO_2^+$ has been the subject of controversy.[1] In a ^{15}N NMR study of aqueous nitrite, a resonance was observed ca. 200 ppm upfield from HNO_2 and assigned to $H_2NO_2^+$.[3] This apparently large shielding has been cited as evidence for protonation at nitrogen,[4] although theoretical studies suggest that only O-protonation would be expected to occur in this assumed species.[5,6] Prakash *et al.*[7] have presented persuasive chemical shift and line broadening evidence that NO^+ formation in this system *does* occur via a distinct nitrous acidium species, which they formulate as "$HNO_2{\cdot}H_3O^+$". In their interpretation, this consists of three equilibrating species (or, in their words, is a "resonance hybrid" of three structures), in one of which a proton is covalently bound to nitrogen. The question of N-protonation has been addressed in the present study by NOE measurements.

An additional major objective of the present study is to achieve reliable determination of the protonation shielding for nitrite ion. Chemical shift measurements reported by Lown *et al.*[8] for $Na^{15}NO_2$ in aqueous acetone treated with HCl at various concentration and acidity levels show an apparent, gross shift in the range 30–40 ppm. The systems employed in those measurements lacked definition, however, due to the well-known disproportionation reaction (eq 4). From the forward rate law

$$3HNO_2(aq) \rightleftarrows 2NO(g) + H^+(aq) + NO_3^-(aq) + H_2O \qquad (4)$$

for this reaction (eq 5),[9] it is seen that in principle the initial rate

$$-d[HNO_2]/dt = k_f([HNO_2]^4/P_{NO}^2) \qquad (5)$$

should be infinite in the absence of NO and the composition of the system should be subject to substantial variability during NMR acquisition time. The measurements in question also appear to have been carried out in open systems, with consequent probable loss of nitrogen to the gas phase and uncontrolled equilibrium shifts. In the present study, chemical shift measurements have been carried out in closed, NO-pressurized systems.

Prakash *et al.* have also explored the ^{15}N NMR spectroscopy of nitrate in D_2SO_4 solution,[7] following up the earlier ^{14}N NMR study of Ross *et al.*,[10] and report a slow nitrogen exchange between NO_2^+ and NO^+ in sulfuric acid solution. Limited measurements on these species in solution have been included in the present study, and solid-state ^{15}N NMR spectra have been obtained at natural abundance for both NO^+ and NO_2^+ in the presence of BF_4^- as counterion.

Experimental Section

Samples were prepared for NMR measurement by adding 10 mg of $Na^{15}NO_2$ (Stohler, 95 atom % ^{15}N) to 0.40 mL of argon-deaerated aqueous

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buffer solution, held frozen at 195 K in an NMR tube, which was then attached to a vacuum system and pumped to $<10^{-4}$ Torr. Nitric oxide was purified by repeated distillation from 5-Å molecular sieves at 113 K to a trap at 77 K followed by pumping. A measured quantity of this gas, in an amount calculated to yield approximately 1 atm of pressure at the anticipated final volume and 273 K, was transferred quantitatively into the NMR tube by condensation at 77 K. With its contents held continuously at that temperature, the tube was then drawn down with a torch and sealed at a point designed to leave ca. 0.1 mL of free gas space above the condensed phase. Sealed samples were held frozen at 253 K until inserted in the NMR probe. High acidity samples were prepared by thorough argon purging of a quantity of the acid of interest ($HClO_4$, H_2SO_4, or D_2SO_4) in an NMR tube fitted with a septum, followed by slow injection of deaerated $Na^{15}NO_2$ (or $H^{15}NO_3$) solution, at appropriate concentration and volume, beneath the liquid surface.

Potassium hydrogen phthalate buffers were used in the pH range 2.2–2.8, and citric acid buffers in the pH range 3.0–5.0, all at ionic strength ca. 0.5 M. The pH for each point was established by direct measurement on 0.40 mL of buffer containing 10 mg of dissolved $NaNO_2$. Additional measurements at the same nitrite concentration level (0.36 M) were carried out in 0.1 M NaOH, unbuffered H_2O (pH 8.4), 20% (w/w) $HClO_4$, 42.4% and 44.9% D_2SO_4, 70% $HClO_4$, 70% H_2SO_4, and ca. 95% H_2SO_4. Chemical shift measurements were also carried out on $H^{15}NO_3$ at 0.1 M concentration in H_2O and 70% $HClO_4$. NOE measurements were carried out for $Na^{15}NO_2$ at pH 3 and in 20% and 70% $HClO_4$ solutions, all at conditions essentially similar to those given above except for the inclusion of 10% D_2O, and in 99% D_2O containing 42.4% D_2SO_4.

Samples at −20 °C were inserted into the NMR probe, where the temperature was gradually raised to 2 °C. Acquisitions were begun following an interval (ca. 5 min) sufficient to accomplish thawing, homogenization, and thermal equilibration. To permit replication, samples were returned to and held at 253 K upon completion of measurements.

Using the rate law in eq 5 and rate constant value $k_f = 0.602$ L^3 atm^2 mol^{-3} min^{-1} at 0 °C,[11] the initial HNO_2 decomposition rate is found to be $\leq 5.5 \times 10^{-3}$ mol L^{-1} min^{-1} for our weak acid conditions (pH $\geq$ 2.2) and 1 atm NO. Therefore, for most of these systems little decomposition would have occurred during normal acquisition times (ca. 20 min). Using the values $\Delta H = 49.7$ kJ and equilibrium constant $K_{303} = 39.6$ L atm^2 mol^{-1} for reaction 4,[11] we find $K_{275} = 5.3$ L atm^2 mol^{-1} and calculate that at full equilibration the maximum HNO_2 decomposition for our systems at pH $\geq$ 2.2 would have been about 70%.

Chemical shift measurements were performed using a Bruker MSL-400 NMR spectrometer operating at a frequency of 40.55 MHz for ^{15}N. The data were collected using a solenoidal coil single frequency probe. Temperature was regulated to ±0.5 °C using a stream of cooled nitrogen gas. Spectral widths of 8000 Hz were collected, with a resulting digital resolution of approximately 1 Hz. The pulse width was maintained at 10 μs (45° flip angle) with a relaxation delay between scans of 6 s. Typically 32–256 scans were acquired for each sample.

Equilibrium nitrogen-proton nuclear Overhauser enchancement (NOE) values were determined from data collected on a Bruker AC-250 spectrometer operating at a frequency of 250.13 MHz for protons with a corresponding ^{15}N frequency of 25.346 MHz. The data were collected using a 10-mm broad-band probe with the observe coil turned to the ^{15}N frequency. The temperature was regulated with a stream of cooled nitrogen gas and maintained to ±0.2 °C. Spectral widths of approximately 5000 Hz (10 000 at 42.4% D_2SO_4) comprised of 32 000 data points were collected, with a resulting digital resolution of approximately 0.3 Hz (0.6 for 42.4% D_2SO_4). A 90° pulse (21.5 μs) for ^{15}N was employed. A relaxation delay greater than 10 times estimated T_1 was placed prior to each scan (100 s in the case of 42.4% D_2SO_4, 300 s in the others). Broad-band proton decoupling was applied during all acquisition times and during the relaxation delay for data with NOE. Data were collected in an interleaved mode, in which data with and without NOE were collected sequentially and the cycle was repeated after eight scans to minimize any error due to sample decomposition. Typically 32 scans were collected in this manner for all but the 42.4% D_2SO_4 measurement, in which case 512 scans were required to achieve an acceptable S/N ratio, due to exchange broadening.

All solution-state NMR measurements were referenced with respect to liquid NH_3, using external 1.0 M $H^{15}NO_3$, with the assigned chemical shift value 375.8 ppm.[12]

Table I. Variation of ^{15}N Chemical Shift with Acidity in the Nitrite–Nitrous Acid System at 2 °C[a]

pH	f[b]	$\delta(^{15}N)$, nitrite/ppm[c]	$\delta(^{15}N)$, nitrate/ppm[c]
13	0	609.4	
8.4	0	609.3	
5.0	0.012	609.0	
4.8	0.019	608.9	
4.6	0.030	608.3	
4.4	0.047	607.6	
4.2	0.072	607.2	
4.0	0.110	606.0	
3.8	0.163	604.3	
3.6	0.236	602.6	
3.4	0.329	599.5	
3.2	0.437	596.3	
3.0	0.552	593.4	375.8
2.8_3	0.645	591.1	
2.6_5	0.734	587.1	
2.2_2	0.881	582.6	374.8

conditions	$\delta(^{15}N)$, nitrite/ppm	$\delta(^{15}N)$, nitrate/ppm[c]
20% $HClO_4$	576.2	
42.4% D_2SO_4 (HNO_2)	569.5	
42.4% D_2SO_4 (NO^+)	359.1	
44.9% D_2SO_4 (HNO_2)[d]	567.2	
44.9% D_2SO_4 (NO^+)[d]	357.8	
70% $HClO_4$	386.3	
70% $HClO_4$[e]	386.5	344.3
70% H_2SO_4	388.7	
95% H_2SO_4	378.9	
$NO^+BF_4^-$ (solid state)	379.1	

[a] Total nitrite $[HNO_2] + [NO_2^-] = 0.36$ M. [b] Fraction of NO_2^- protonated, based on pK_a = 3.09. [c] Measured relative to 1 M HNO_3, reported relative to NH_3(l); correction factor = 375.8.[12] [d] Total nitrite = 1.0 M. [e] Duplicate system and measurement (see text).

Solid-state NMR measurements were carried out at a field of 7.1 T (30.554 MHz ^{15}N frequency) using a home-built spectrometer. NO_2BF_4 was obtained from Fluka Chemical Co., Ronkonkoma, NY, and $NOBF_4$, from Aldrich Chemical Company, St. Louis, MO; both were used without further purification. They were sealed in a 7 mm sample rotor in an inert atmosphere. Magic-angle spinning spectra were obtained without cross-polarization or dipolar decoupling, by Fourier transformation of a simple Bloch decay. These latter were collected using a 3.5-μs ^{15}N pulse (flip angle approximately 60°), a sample window of ±20 KHz, and recycle delays of 120 s; 1440 transients were averaged for each spectrum of $NOBF_4$ and 2880 for NO_2BF_4. Spectra were collected at two or three rotor frequencies in order to confirm the identification of the isotropic frequency and to give an estimate of the shielding anisotropy. Solid-state measurements were referenced to 5.6 M NH_4Cl in H_2O, as a secondary reference, and were not corrected for susceptibility effects, which are expected to be small.

Chemical shielding anisotropies were estimated from the MAS sideband patterns by standard methods. The signal to noise ratio permitted these to be estimated to about 10% accuracy.

Results and Discussion

Values of $\delta(^{15}N)$ for nitrite, measured at close intervals over the protonation range pH $\geq$ 2.2, are shown in Table I, along with corresponding values of f, the protonated fraction of total nitrite ($f = [HNO_2]/\{[HNO_2]) + [NO_2^-]\}$). These were calculated using the value pK_a = 3.09 for HNO_2, taken from the data of Tummavuori and Lumme[13] corrected to $T = 275$ K using their value $\Delta H = 15.9$ kJ and to $I = 0.5$ M using the formulation of Castro *et al.*[14] The table also shows the presence of disproportionation nitrate observed at low concentration levels in two of the low acidity samples.

As shown in Figure 1 $\delta(^{15}N)$ varies with strict linearity in f over the pH range 2.2–5.0. The extrapolated value at $f = 1.0$

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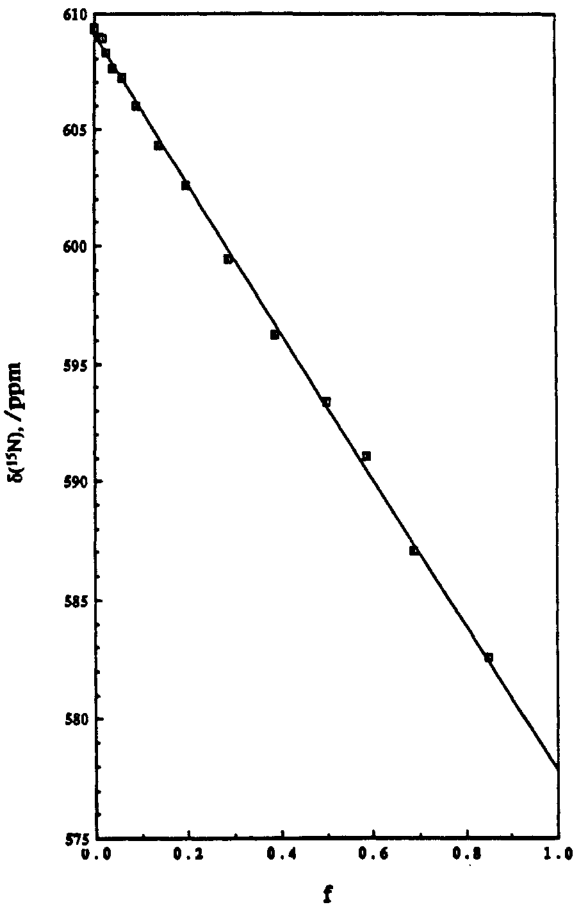

Figure 1. Dependence of chemical shift on protonation fraction in the HNO_2–NO_2^- system at 2° C.

should therefore correspond to $\delta(^{15}N)$ for the fully protonated molecule HNO_2. Linear regression for these 14 points (correlation = 0.9991) yields the result $\delta(^{15}N) = 579.6$, for a total protonation shielding $\Delta\delta(^{15}N) = -29.7$ ppm (upfield) for NO_2^-. The value $pK_a = 3.09$ used above is uncertain due to a strong temperature dependence of ΔH;[13] when the data of Table I are plotted as a titration curve, the graphically estimated value $pK_a = 3.0$ is obtained. A plot of $\delta^{15}N$ vs f based on this result shows a slightly improved correlation and yields the extrapolated value $\delta(^{15}N) = 577.9$ ppm, i.e. $\Delta\delta(^{15}N) = -31.0$. In view of the uncertainities intrinsic to both methods it seems reasonable to report the mean of these values, −30.4 ppm, for $\Delta\delta(^{15}N)$. This value is closely similar to the shift of −28.6 ppm recently reported for O-protonation of the anion of *N*-hydroxybenzenesulfonamide, $C_6H_5SO_2NHO^-$.[15]

Our value $\delta(^{15}N)$ for $NaNO_2$ in aqueous solution (Table I) is in agreement with those of Lambert and Roberts[16] and of Prakash *et al.*[7] The linearity of Figure 1 indicates a continuity of equilibrium states between NO_2^- and HNO_2 over the pH interval involved, without significant participation of additional equilibria capable of introducing new species, e.g. NO^+ or $H_2NO_2^+$. The formation constant for NO^+ has been reported to lie in the range 2.5×10^{-7} to 8×10^{-9} L mol^{-1} at 25 °C,[17] and NO^+ concentrations are expected to be extremely small at low acidity. Table I also shows $\delta(^{15}N)$ values for nitrite in 20% and 70% $HClO_4$, 70% and 95% H_2SO_4, and 44% D_2SO_4. Our value for HNO_2 in 20% $HClO_4$ (576 pm) is slightly lower than the $f = 1.0$ value and is in agreement with values of Prakash *et al.* in 10–20% D_2SO_4 at −5 °C (575 ppm). We also observed the slight broadening reported by these authors, which they interpret as due to exchange equilibrium between HNO_2 and the nitrous acidium ion. We assume that the slight drop in $\delta(^{15}N)$ from its extrapolated ($f = 1.0$) value is due to the same cause. Our values in 70% $HClO_4$ (386 ppm) and in 70% H_2SO_4 (389 ppm) and (ca.) 95% H_2SO_4 (379 ppm) reflect the predominance of NO^+ under these conditions. The 70% $HClO_4$ value was remeasured on an entirely distinct duplicate system, using the AC-250 rather than MSL-400 spectrometer, with the closely matching result shown. In this single case a trace of nitrate, not seen in other high acidity samples, was detected.

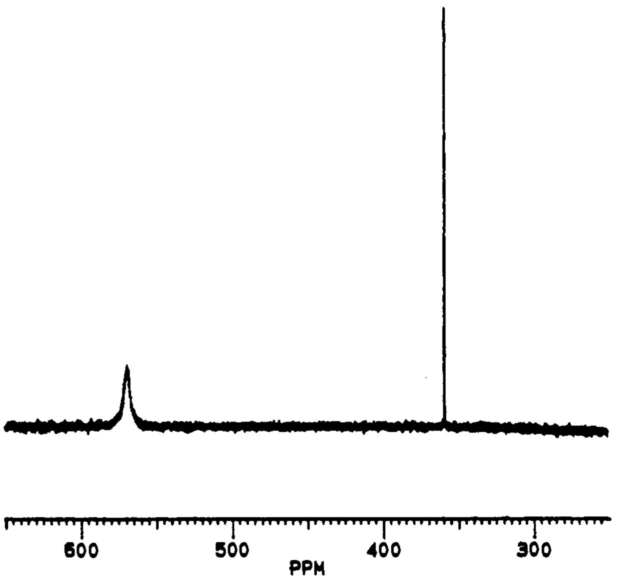

Figure 2. ^{15}N NMR spectrum of $NaNO_2$ (0.36 M) in 42.4% D_2SO_4.

As expected from the results of Prakash *et al.*,[7] we observed two resonances in 42.4 and 44.9% D_2SO_4, one (broad) assignable to HNO_2, the second (sharp) to NO^+ (see Figure 2). The observed chemical shift values at these concentrations fit appropriately between those reported by Prakash *et al.* for 40% and 50% D_2SO_4. The blue color of these solutions, also observed by Prakash *et al.*, indicates the presence of N_2O_3, a condition related to the known occurrence of maximum nitrite decomposition rate in this acidity range.[2d] Our high acidity results are in satisfactory agreement with the values of Prakash *et al.* for nitrite dissolved in HSO_3F (383 ppm) and in 98% D_2SO_4 (377 ppm), and fit well in turn with our own solid-state NMR result for $NOBF_4$ (379.9 ppm; *vide infra*).

In addition to resonances correctly assigned to HNO_2 by Lown *et al.*,[8] many of the results reported by these authors for $Na^{15}NO_2$ solutions at varying acidity levels exhibited additional, unassigned resonances. The most frequently occurring of these, at ca. 376 ppm, are assignable to HNO_3 resulting from the disproportionation reaction (eq 4). The resonance assigned to $H_2NO_2^+$ (354 ppm in ref 3; 361 ppm in ref 8) clearly corresponds to NO^+. The initial acidity of the solutions employed in these experiments was much lower than the level to which these values correspond, but the use of open systems could have yielded detectable NO^+ since extensive disproportionative NO loss would increase both acidity and nitrate concentration (eq 4).

From the formation constant for N_2O_3 reported by Markovits *et al.* (3.3×10^{-3} L mol^{-1} at 22 °C),[18] we estimate that the maximum concentration of this species in our systems at low acidity, where it plays a known role in nitrosation,[1] would have been in the range 10^{-4}–10^{-5} M. With increasing NO^+ concentration, formation of N_2O_3 to substantial levels is expected,[2d] and the appearance of this species is confirmed by the blue color of nitrite solutions in 40–50% D_2SO_4. Nitrogen-15 resonances for

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Table II. ^{15}N Chemical Shift for HNO_3 in Solution and NO_2BF_4 in the Solid State

system	$\delta(^{15}N)$/ppm
0.1 M HNO_3 in H_2O	375.7[a]
0.1 M HNO_3 in 70% $HClO_4$	346.7
$NO_2^+BF_4^-$ (solid state)	252.3[b]

[a] Measured relative to 1 M HNO_3, reported relative to NH_3(l); correction factor = 375.8.[12] [b] Measured relative to 5.6 M NH_4Cl, reported relative to NH_3(l); correction factor = 27.3 ppm.[12]

N_2O_3 in CH_2Cl_2 solution at −100 °C have been reported at 645 ppm (nitroso nitrogen) and 416 ppm (nitro nitrogen), relative to a NH_4Cl solution of unspecified concentration.[19] No resonance that could be ascribed to N_2O_3 was reported by Prakash *et al.*, and although our measurement at 42.4% D_2SO_4 was carried out in a spectral window covering the range 325–650 ppm, we detected no sign of an N_2O_3-assignable resonance. A resonance reported at 413 ppm in four of the solutions of ref 7, however, may possibly have been due N_2O_3.

In view of the suggestion that the species $H_2NO_2^+$ involves protonation at nitrogen,[4] we carried out NOE measurements at pH 3, in 20% and 70% $HClO_4$ and in 42.4% D_2SO_4. No NOE was detected at any of these four conditions, and we conclude that no direct proton-to-nitrogen connectivity occurs. The extensive exchange broadening observed for the HNO_2 peak at 42.4% D_2SO_4 makes this condition optimal for the presence of some form of nitrous acidium ion, but even here no NOE was detected, within the (small) error of measurement. This result raises some question about the form of the $HNO_2{\cdot}H_3O^+$ species postulated by Prakash *et al.*[7]

Our limited chemical shift measurements for HNO_3 in water and in strong acid (Table II) show the expected shift associated with NO_2^+ formation. To confirm assignments to NO^+ and NO_2^+, solid-state ^{15}N NMR spectra were obtained for the fluoroborates $NOBF_4$ and NO_2BF_4 at natural abundance (see Figure 3). These spectra illustrate that, even without signal enhancement from isotope enrichment or cross-polarization and in samples with long longitudinal relaxation times, usable ^{15}N spectra can be obtained for solids of low molecular weight within feasible acquisition times.

The spectra in both cases contain isotropic centerbands flanked by rotational sidebands: these sidebands both confirm that the resonances arise for solid material, rather than liquid contaminants, and provide additional information in the form of chemical shift anisotropies. The isotropic chemical shift values are shown in Tables I and II. The value for NO^+ (379.1 ± 2 ppm) is in adequate agreement with our result at 70% $HClO_4$ when the likely incomplete formation of NO^+ in the solution system and the intrinsic difference between the solid state and aqueous nitrogen environments are taken into account. It is also in satisfactory agreement with the value 376.9 ppm for $NOBF_4$ in SO_2 solution reported by Olah *et al.*[20] (measured vs 2 M $NaNO_3$, here corrected to $\delta(NH_3) = 0$) and the results of Prakash *et al.*[7] Our value for NO_2^+ (252.3 ± 2 ppm) is in satisfactorily close agreement with the measured values $\delta(^{15}N) = 248.7$ ppm (+127.8 vs 2 M $NaNO_3$) reported by Olah *et al.* for NO_2BF_4 in SO_2 solution[20] and 251 ppm reported by Prakash *et al.* for $Na^{15}NO_3$ in 98% H_2SO_4.[7]

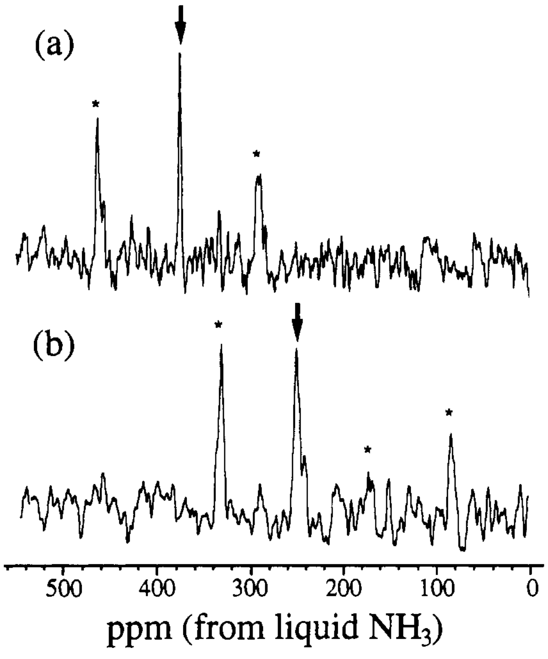

Figure 3. (a) Magic angle spinning spectrum of $NOBF_4$, obtained at a Zeeman frequency of 30.55 MHz and a rotational frequency of 2.7 KHz. (b) Magic angle spinning spectrum of NO_2BF_4, obtained at the same Zeeman frequency and a rotational frequency of 2.5 KHz. In both spectra, rotational sidebands are marked with an asterisk and center bands with an arrow. (The position of the $N = 1$ sideband is marked, even though its intensity is very small.)

The sideband patterns for NO_2BF_4 were fit to an axially symmetric tensor with an anisotropy $(\sigma_{11} - \sigma_{33})$ of 360 ± 40 ppm. The unique principal value, which by symmetry corresponds to the long axis of the molecule, is the most shielded. This value may be compared with the CSA of NO_3^-, which is considerably smaller, approximately 200 ppm.[21,22] The shielding anisotropy of nitrosonium is similar in sign and magnitude; we obtain a value of 400 ± 40 ppm for this quantity. It should be noted that in this respect the nitronium cations do not follow the trend of the corresponding oxyanions, where the nitrite shielding anisotropy is considerably greater than that of nitrate.

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