Temperature dependence of the ^{15}N and ^{1}H nuclear magnetic shielding in NH_3

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The temperature and density dependence of the ^{15}N and the ^{1}H nuclear resonance in $^{15}NH_3$ gas have been observed. The density dependence which is a measure of the effect of intermolecular interactions on the nuclear shielding is linear, with slopes of -0.041 ± 0.002 ppm/amagat for the ^{15}N nucleus and -0.0032 ± 0.0001 ppm/amagat for the ^{1}H nucleus. The shielding in the limit of zero pressure σ_0 varies with temperature due to rovibrational motion. This is of special interest for the ^{15}N shielding in NH_3 because of the previously reported exceptional temperature dependence of ^{31}P in PH_3. It is found that ^{15}N in NH_3 is also an exceptional case and, in fact, near 300 K ^{15}N in NH_3 and ^{31}P in PH_3 have nearly identical values of $d\sigma_0/dT$ ($+0.00651 \pm 0.00082$ ppm/deg for ^{15}N in NH_3 from 320 to 380 K). All other cases, involving a variety of nuclei in a wide variety of molecular types, exhibit $d\sigma_0/dT < 0$.

INTRODUCTION

The observed resonance signal for a nucleus in a molecule in the gas phase is affected by intermolecular encounters and also by rotational–vibrational motion. Both effects are functions of temperature, so the nuclear magnetic shielding may be expressed as an expansion in powers of density as follows:

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \cdots, \quad (1)$$

where ρ is the density of the gas and $\sigma_1(T)$ is a measure of the effects on nuclear shielding due to binary collisions, whereas $\sigma_0(T)$ is the temperature dependent shielding in the limit of zero pressure. The latter function is a measure of the effects of vibrational averaging and centrifugal distortion on the nuclear shielding.

We have investigated the $\sigma_0(T)$ and $\sigma_1(T)$ functions for nuclei in several types of simple molecules such as diatomics, AX_2 types, tetrahedral AX_4, planar and pyramidal AX_3, octahedral AX_6, as well as symmetric tops such as AYX_3.[1] The ^{19}F nucleus has proved to be the most useful probe of the effect of intramolecular dynamics on shielding [in terms of the $\sigma_0(T)$ function] due to its high sensitivity and very large shifts. We are able to obtain well-defined $\sigma_0(T) - \sigma_0$ (300) functions for ^{19}F with high relative precision.[1-3] Results with other nuclei such as ^{15}N, ^{13}C, ^{11}B, and ^{31}P have been less satisfactory,[1,4-10] not entirely due to their lower sensitivity. Our observation that more centrally located nuclei tend to have smaller temperature coefficients of σ_0 than peripheral nuclei such as fluorine accounts for part of the difficulty. However, since ^{19}F nuclei are unlikely to be found as the apical nucleus in a pyramidal AX_3 or the central nucleus in any of AX_2, AX_3, AX_4, or AX_6 types of molecules, the less sensitive nuclei are the only available probes of the vibrational and rotational effects on the shielding of a nucleus so situated. Thus, we have observed ^{13}C and ^{15}N in molecules such as CO, CO_2, and NNO.[8,11] The temperature coefficients of σ_0 for these nuclei have been found to have the same sign as ^{19}F. While ^{13}C and ^{11}B in CH_4 and BF_3 exhibited no measurable temperature dependence in the limit of zero pressure,[6,10] we have found in all other systems that $d\sigma_0/dT$ has the same sign (negative) with one notable exception, that of ^{31}P in PH_3.[9] Other ^{31}P nuclei (in PF_3, POF_3, and PF_5) did not exhibit this exceptional behavior.[1]

Our ^{31}P in PH_3 results suggest that σ_0 for apical nuclei in some other trigonal pyramidal molecules might behave unusually. Of the possible systems to study (PF_3, NH_3, and NF_3), NH_3 is a natural choice. ^{31}P in PF_3 did not exhibit the unusual temperature dependence found in PH_3 so ^{15}N in NF_3 is less likely to be an exception. In this paper we report our results for ^{15}N in NH_3. We find the ^{15}N in NH_3 to be the second exceptional case in which $d\sigma_0/dT$ is positive and the temperature coefficient of σ_0 is virtually the same as that of ^{31}P in PH_3. This result is of theoretical significance because, unlike PH_3, NH_3 has a sufficiently small number of electrons for a realistic theoretical calculation of the dependence of the nuclear magnetic shielding of the ^{15}N and the ^{1}H nuclei upon N–H bond displacement and HNH angle deformation.

EXPERIMENTAL RESULTS

Sealed samples of 99% ^{15}N labeled ammonia with measured densities ranging from 12 to 40 amagat were placed in a 5 mm NMR tube containing the liquid lock substance. The ^{2}D resonance signal of CD_3 group in toluene-d_8 was used as the external reference to stabilize the magnetic field. The temperature dependence of the liquid reference is known from earlier work.[12] Due to the low sensitivity of ^{15}N, no sample densities below 12 amagat were used. Thus, the temperature range covered is narrower than usual due to the relatively high temperatures (300–350 K) at which the saturated vapor density equals 10–40 amagat.[13]

^{15}N

Pulsed Fourier transform NMR spectra were observed with a Bruker spectrometer operating at a field

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strength of 21 kG equipped with a variable temperature controller and a Nicolet 1080 data acquisition system. The ^{15}N spectra were taken with a sweep width of 1000 Hz, requiring 256 to 2500 transients depending on the density of the sample. Typical repetition rates were 2.2 s. Linewidths of individual peaks were 1 Hz. The $^{15}N-^{1}H$ coupling constant observed in NH_3 gas was $|61.7 \pm 0.2|$ Hz, which is in agreement with the literature value for the liquid.[14] Any density or temperature dependence of the coupling constant was small and within experimental error. ^{1}H decoupling experiments offered no significant advantage. Although the intensities of each of the two inner peaks in the quartet were about half of the decoupled signal, they provided two independent measures of the center position and their frequency separation provided a check on the assignment of the signal. At these low signal to noise ratios, this is a distinct advantage over a single peak. Sample preparation, temperature regulation, and sources of error have been discussed earlier.[15,16]

The observed frequencies at 9.119 MHz are shown in Fig. 1, where inner peaks are plotted as $\nu_{obs} \pm J/2$ and outer members of the quartet, when observable, as $\nu_{obs} \pm 3J/2$. The data are consistent with a constant σ_1 value equal to that obtained by observing samples of various densities at the same temperature (350 K). The solid lines indicate the expected frequencies for a temperature independent σ_1 equal to -0.041 ± 0.002 ppm/amagat. When the effect of the density dependence

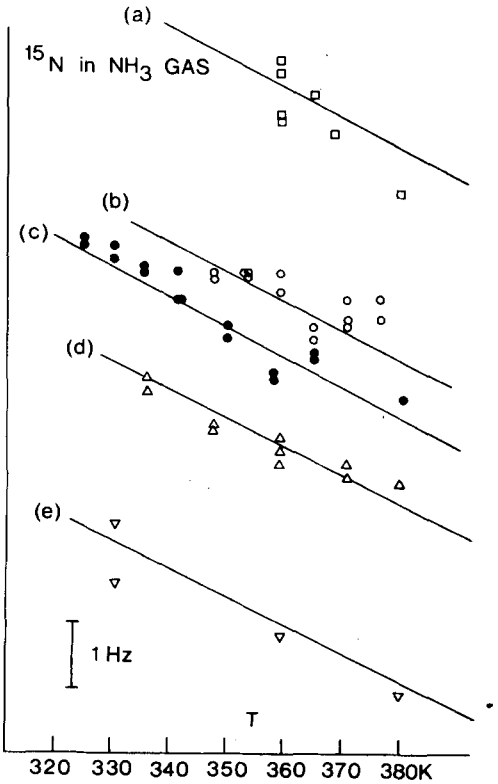

FIG. 1. ^{15}N resonance frequencies at 9.119 MHz in NH_3 in the gas phase. Densities of samples are (a) 32.94, (b) 24.65, (c) 22.25, (d) 18.70, (e) 12.38 amagat. The solid lines are drawn to be consistent with the $\sigma_1 = 0.372$ Hz/amagat measured from all samples at 350 K.

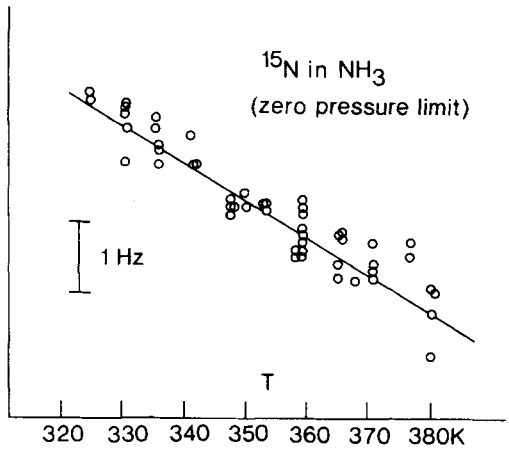

FIG. 2. ^{15}N resonance frequencies at 9.119 MHz in the limit of zero pressure.

of the gas is removed from each sample as $\sigma_1\rho$, and the precisely known temperature dependence of the reference substance is subtracted out, the remaining temperature dependence is a measure of $\sigma_0(T)$. The results from all samples are combined and are shown in Fig. 2. Fitted to a straight line, this gives a slope of -0.0594 Hz/deg. Thus, $\sigma_0(T) - \sigma_0(300) = +0.00651 \pm 0.00082\ (T-300)$ ppm for $T = 320-380$ K.

Figure 1 shows only the results for the gas phase. Both liquid and vapor signals were observed at lower temperatures for each of the samples (except the 12.38 amagat sample). The liquid phase spectrum was always a single peak, somewhat broader than the individual members of the vapor phase quartet, as seen in Fig. 3. This was expected from the similarity with ^{17}O in liquid H_2 ^{17}O in which the line is "exchange narrowed," the proton exchange being fast enough for the averaging of the individual resonance frequencies to occur.[17] The frequency of the liquid signal showed a linear behavior with temperature over the range 300–360 K with a slope of 0.068 ppm/deg. This appeared to be in disagreement with the earlier observations of Litchman, Alei, and Florin,[18] who report a linear temperature dependence in the liquid phase with a temperature coefficient of 0.0442 ± 0.001 ppm/deg (significantly smaller than ours) over the range 203–303 K. To resolve this apparent discrepancy we observed the ^{15}N resonance in liquid NH_3 from 207–358 K. We found that the data, shown in Fig. 4, could indeed be fitted to a straight line over a narrow range of temperature such as 50 K. However, there is significant curvature which is outside of experimental error. Litchman, Alei, and Florin's smaller temperature coefficient for 203–303 K is consistent with the low temperature end, whereas our larger temperature coefficient for 300–360 K is consistent with the high temperature end of the curve. The discrepancy is not a real one. The temperature dependence of the ^{15}N resonance signal in liquid NH_3 under its own vapor pressure is adequately described by $\sigma(T) = \sigma(300) + 0.0605(T-300) + 0.111 \times 10^{-3}(T-300)^2$ ppm from 207 to 358 K.

The vapor signals from the spectra of samples with liquid–vapor equilibria also contain the same informa-

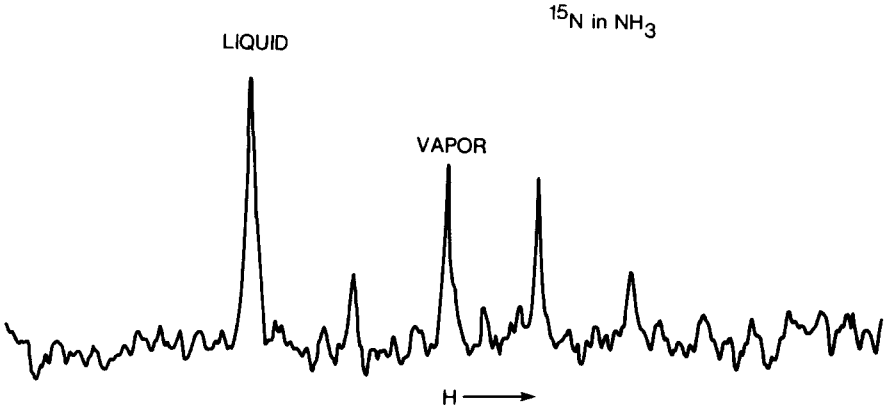

FIG. 3. A ^{15}N spectrum showing both the vapor phase and the liquid phase spectra in a sample with liquid–vapor equilibrium.

tion as the separate gas phase samples, except that the temperatures and densities are not independently variable. The independently measured $d\sigma_0/T$ and the temperature dependence of the reference were used to "correct" the vapor phase frequencies at each temperature such as to leave only the density dependent part. The plot of these frequencies versus the vapor densities from Landolt-Bornstein tables[13] gives a value of σ_1 for ^{15}N which is -0.047 ± 0.005 ppm/amagat, a value indistinguishable from -0.041 ± 0.002 ppm/amagat obtained using low density gas samples.

The gas-to-liquid shifts observed in samples with liquid–vapor equilibrium were fitted to a straight line (there was no significant curvature within a 50 K range): $\nu_{liq} - \nu_{vap} = 177.55 - 0.9135(T-300)$ Hz for $T = 298$–350 K. Thus, $(\sigma_{liq} - \sigma_{vap} = -19.47 + 0.1002(T-300)$ ppm for ^{15}N in NH_3 in liquid–vapor equilibrium. There are several values previously reported for the ^{15}N gas-to-liquid shift in NH_3: -17.20 ppm at 302.2 K,[18] -18.04 ppm at 302.2 K for $^{15}ND_3$,[18] -15.9 ppm at 302.8 ± 0.5 K (incorrectly corrected for susceptibility),[19] and promptly corrected to -18.0 ± 0.2 at the same temperature by the authors,[20] and -22.6 ppm at 195.5 K.[21] Unfortunately, the -15.9 ppm value is most often quoted.[22,23] Our results are uncorrected for bulk susceptibility and are measured by observing both liquid and vapor signals in the same spectrum (see Fig. 3). It is possible that the discrepancy between the results of Litchman *et al.* and ours is partly due to nonreproducible temperatures in some spectrometers (we already noted the large nonlinear temperature dependence of the liquid), and partly due to slightly different bulk susceptibility contributions to the shift.

^{1}H

^{1}H spectra were taken on the same spectrometer at 89.998 MHz. 10–30 transients were adequate for ^{1}H spectra, depending on the density of the NH_3 sample. Proton linewidths of 3–5 Hz were observed in the gas phase. In the liquid, a single broader peak is observed, as in the ^{15}N spectra. Experimental results for ^{1}H are shown in Fig. 5. The temperature and density dependent shifts of ^{1}H nuclear magnetic shielding are much smaller than those of any other nucleus. Thus, it is

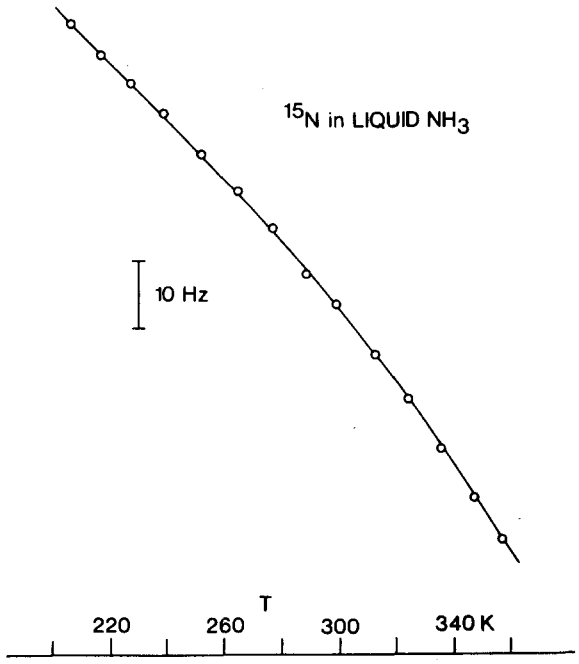

FIG. 4. ^{15}N resonance frequency in liquid NH_3.

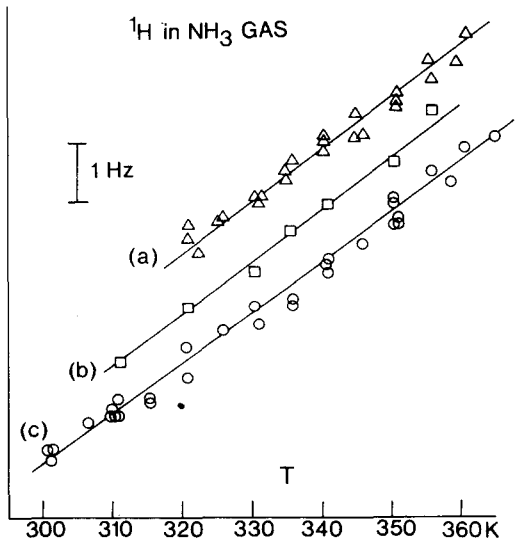

FIG. 5. ^{1}H resonance frequencies at 90.0 MHz in $^{15}NH_3$ in the gas phase. Densities are (a) 18.70, (b) 15.41, (c) 12.38 amagat.

TABLE I. ^{15}N gas to liquid shifts observed at 9.119 MHz.

T	ρ_{liq}[a] (amagat)	ρ_{vap}[a] (amagat)	$\nu_{liq}-\nu_{vap}$ observed (Hz)	σ_1 (apparent)[b] (ppm/amagat)
300	789.50	10.85	177.6	−0.025
310	769.18	14.51	168.4	−0.024
320	747.63	19.09	159.3	−0.024
330	724.90	24.90	150.1	−0.024
340	700.66	32.20	141.0	−0.023

[a]Landolt-Bornstein, *Zahlenwerte und Funktionen* (Springer, Berlin, 1966), Vol. IV, Part 4a.
[b]Apparent $\sigma_1 = -[(\nu_{liq}-\nu_{vap})/9.119(\rho_{liq}-\rho_{vap})]$.

not possible to obtain the same relative precision as we have obtained for ^{15}N or ^{19}F data despite the greater absolute precision of our ^{1}H spectra. We could find no measureable temperature dependence in the σ_1 of ^{1}H in NH_3; we report a value of -0.0032 ± 0.0001 ppm/amagat for 300–370 K. The temperature dependence in the zero pressure limit is very small. We find σ_0 for ^{1}H in NH_3 to be a linear function of temperature $\sigma_0(T) - \sigma_0(300) = -4.08\times10^{-4}\ (T-300)$ ppm for 300–370 K. The gas-to-liquid shift $(\sigma_{liq}-\sigma_{vap}) = -1.75$ ppm at 300 K and the temperature dependence of the ^{1}H resonance signal in liquid NH_3 under its own vapor pressure is similar to that for ^{15}N (Fig. 4). Fitted to a polynomial, the function is $\sigma(\text{liq}, T) = \sigma(\text{liq}, 300) + 0.01050(T-300) + 2.70\times10^{-5}\ (T-300)^2$ ppm from 220–320 K. This is a much greater temperature dependence than was earlier reported by Alei and Florin for the range 240–300 K.[24]

Because of the greater sensitivity of ^{1}H compared to ^{15}N nuclei, measurements of $^{1}H-^{15}N$ coupling from ^{1}H spectra could have resulted in sufficiently precise data to observe any temperature or density dependence in the $^{1}H-^{15}N$ coupling constant in the gas phase. However, we observed none. The vibrational correction to the $^{1}H-^{15}N$ coupling constant (which would be observed as a temperature dependence) has been the subject of some calculations. A 15% correction in the ground state relative to the equilibrium configuration (9.3 Hz in terms of the observed $^{1}J_{NH}$) was calculated by Solomon and Schulman using MINDO/3.[25] However, the predicted temperature dependence is very small because the inversion doublets which furnish the large corrections have a fairly small population. From these calculations one can predict a 0.20 Hz change in $^{1}J_{NH}$ between 300 and 350 K. This is a large enough change to be observed in ^{1}H spectra. We find the change in $^{1}J_{NH}$ between 300 and 350 K to be less than 0.05 Hz.

DISCUSSION

The expected contribution to σ_1 due to bulk susceptibility such as could be estimated from the molar magnetic susceptibility of $NH_3(-16.5\times10^{-6}$ cm^3/mol[26]) is −0.00154 ppm/amagat. This contribution is the same for all nuclei in the molecule. The observed magnitude of σ_1 for ^{15}N in NH_3 in the gas phase (−0.041 ppm/amagat) is significantly larger than the bulk susceptibility contribution, and larger than that for ^{15}NNO interacting with NNO(−0.01 ppm/amagat) or ^{15}NNO interacting with Xe(−0.02 ppm/amagat). The observed magnitude of σ_1 for ^{1}H in NH_3 in the gas phase (−0.0032 ppm/amagat) is also significantly larger than the bulk susceptibility contribution, and is comparable to the values reported for other protons (e.g., −0.00667 and −0.00771 ppm/amagat for ^{1}H in HCl and HBr, respectively[27]). The σ_1 for both ^{15}N and ^{1}H in NH_3 are the same sign as has always been observed; intermolecular interactions lead to deshielding.

Another measure of intermolecular interactions is the gas-to-liquid shift. Since ternary and higher order encounters are significant in the liquid phase, the magnitude of the apparent σ_1 one might estimate from gas-to-liquid shifts has been smaller than that obtained from $(\partial\nu/\partial\rho)$ in low density gases.[28] Sometimes the difference is within the experimental error in σ_1 ob-

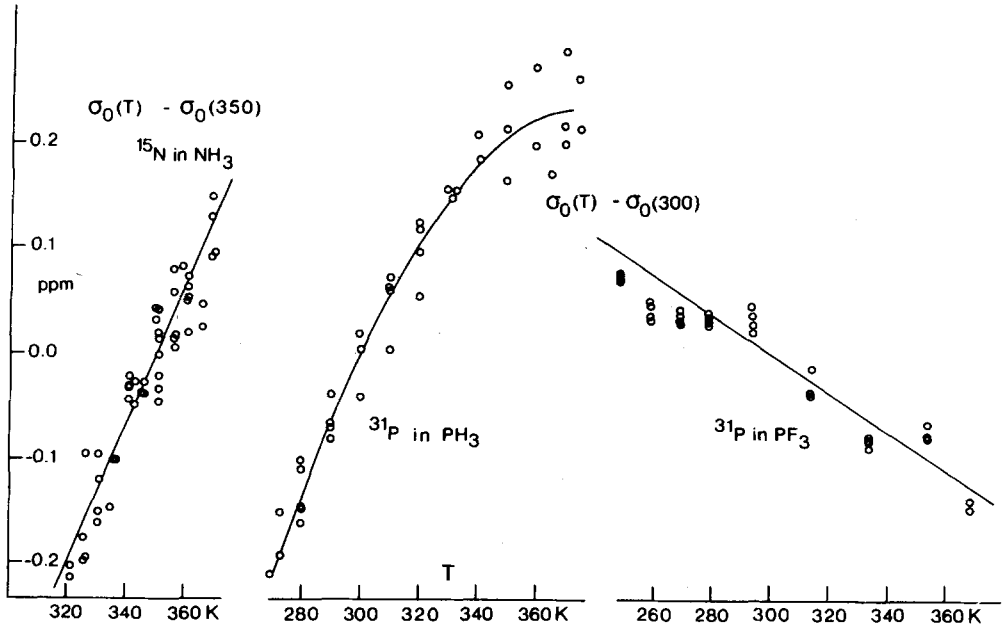

FIG. 6. Comparison of σ_0 (T) of ^{15}N in NH_3 with other AX_3 type molecules.

tained from the gas phase. The gas-to-liquid shifts in NH_3 are considered in Table I. The "apparent σ_1" values for ^{15}N, all about -0.024 ppm/amagat, are indeed smaller than -0.041. It has been suggested that the downfield shifts of the ^{15}N resonance with decreasing temperature in liquid NH_3 could indicate an increase in the extent of hydrogen bonding in the liquid.[18,21] The nearly temperature independent "apparent σ_1" values that we find in Table I indicate that the temperature dependence of the shifts in the liquid are at least partly due to the temperature dependence of the liquid density. It should be noted that temperature dependent studies of intermolecular interactions in the liquid phase at constant pressure, whether in pure liquids or in solution, will always be subject to this problem. A part of what is commonly attributed to temperature dependence of specific or nonspecific association in the liquid phase may be effects due to expansion of the solvent. As has been stressed by Jonas, only constant volume experiments can yield the correct temperature dependent molecular properties in condensed phases.[29]

The $d\sigma_0/dT$ found here for ^{15}N in NH_3 is of the same sign (positive) and magnitude as that of ^{31}P in PH_3; both are exceptional cases. Another apical nucleus in a trigonal pyramidal AX_3 molecule is ^{31}P in PF_3. The $\sigma_0(T)$ for these three cases are compared in Fig. 6. The typical behavior is shown by ^{31}P in PF_3. Like PF_3 all other systems studied so far have shown a negative temperature coefficient for the shielding in the isolated molecule. The magnitude of the $d\sigma_0/dT$ of ^{15}N in NH_3 appears to be about the same as that of ^{31}P in PH_3 above room temperature. The temperature dependence of the ^{15}N NMR signal in NF_3 would be an interesting addition to this set of data on pyramidal molecules.

The theory of the temperature dependence of σ_0 has been given elsewhere.[30,31] For a pyramidal AX_3 molecule the linear terms in the expansion of the shielding with respect to bond displacement and angular distortion give

$$d\langle\sigma\rangle^T dT \simeq (\partial\sigma/\partial\Delta r)_e (d\langle\Delta r\rangle^T/dT) + (\partial\sigma/\partial\Delta\alpha)_e (d\langle\Delta\alpha\rangle^T/dT) + \ldots ,$$

where Δr is the displacement of the AX bond from the equilibrium length and $\Delta\alpha$ is the XAX bond angle deformation. The temperature dependence of the mean displacement $\langle\Delta r\rangle^T$ and the mean bond angle distortion $\langle\Delta\alpha\rangle^T$ depends on the dynamics of the AX_3 molecule. For NH_3 these can be estimated using a model intramolecular force field which is parametrized to be consistent with vibrational–rotational spectroscopic data on this molecule.[32] NH_3 is one of a small number of molecules for which cubic potential constants are available. On the other hand, the derivatives $(\partial\sigma/\partial\Delta r)$ and $(\partial\sigma/\partial\Delta\alpha)$ are theoretically calculable from a study of ^{15}N shielding in NH_3 as a function of molecular configuration. ^{15}N nuclear shielding has to be calculated for two or more geometries with values of R_{NH} displaced from the equilibrium bond length. A similar calculation is needed for two or more geometries with values of the HNH angle around the equilibrium bond angle. Of the pyramidal AX_3 molecules which have been studied by NMR in the gas phase, NH_3 is the best candidate for such calculations since it has only 10 electrons.

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