^{15}N nuclear magnetic shielding scale from gas phase studies

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We have measured the ^{15}N nuclear magnetic resonance frequencies in ^{15}N-labeled molecules ($\underline{N}NO$, $N\underline{N}O$, NH_3, N_2, and HCN) in gas phase samples and also in CH_3NO_2 as neat liquid. By using the previously determined temperature dependence of samples of the these gases at various densities, we are able to reduce the measured frequencies to the zero-density limit at 300 K, and obtain shielding differences between rovibrationally averaged isolated molecules at this shielding measurements from molecular beam studies to provide an ^{15}N absolute shielding scale based on $^{15}NH_3$.

INTRODUCTION

Problems associated with setting up an absolute scale of nitrogen shielding have been raised.[1] Since spin rotation constants for more than one molecule containing nitrogen have been determined, the absolute shielding of nitrogen nuclei in several molecules are independently known. It has been noted that measured chemical shifts between these nuclei in neat liquids at various temperatures do not correspond to the differences between the independent absolute shielding values. Wrackmeyer noted discrepancies of 15 to 24 ppm *outside* of the quoted experimental errors in the absolute shielding derived from spin rotation constants.[1] This is not entirely unexpected, since we have already shown in a previous paper that some gas to liquid shifts can be rather large.[2] However, such apparent discrepancies have been attributed not to necessary corrections (gas to liquid shifts, temperature coefficients of chemical shifts, etc.) such as described in the previous paper, but rather to possible inadequacies in the atom dipole method for calculating the diamagnetic contribution to σ which have been used to obtain absolute shieldings from spin rotation measurements. In order to determine whether the former is indeed a major part of the problem, we have undertaken the measurement of the differences in ^{15}N nuclear magnetic shielding in the molecules of interest (NH_3, HCN, N_2 and both nitrogen nuclei in NNO) in the limit of zero density. These measured differences will correspond to shielding differences between isolated molecules and are therefore more closely related to differences between absolute shielding values derived from spin rotation constants than are the chemical shifts between liquids.

Absolute nuclear shielding information from spin rotation constants

It has been shown by Ramsey and by Flygare that the spin rotation constants and the paramagnetic contribution to the nuclear magnetic shielding are related.[3,4]

$$\sigma^p = \sigma^{SR} + \sigma^{nuc} = \frac{m_p}{2mg_N} \sum_{\alpha=x,y,z} \frac{M_{\alpha\alpha}}{G^{(e)}_{\alpha\alpha}} - \frac{e^2}{2mc^2} \sum_{N'}{}' \frac{Z_{N'}}{r^3_{N'}} (y^2_{N'} + z^2_{N'}) , \qquad (1)$$

in which m_p and m are masses of the proton and electron, g_N is the g factor for the nucleus of interest, $M_{\alpha\alpha}$ is the diagonal component of the spin rotational tensor, and $G^{(e)}_{\alpha\alpha}$ is the rotational constant at the equilibrium configuration. The principal axis system of the inertia tensor has been assumed in the above equation. The second term is the nuclear contribution σ^{nuc}, which depends only on the coordinates and atomic number of all the other nuclei N' in the molecule. The total absolute shielding can then be determined by adding the diamagnetic contribution σ^d, which is obtained from theory, calculated at the nucleus of interest N as the gauge origin:

$$\sigma^d = (e^2/3mc^2) \langle \Psi^0 | \sum 1/r_i | \Psi^0 \rangle . \qquad (2)$$

It is very important to calculate the nuclear terms using the same structure as that used for calculating diamagnetic terms.

Ab initio calculations of the diamagnetic part of the shielding are generally reliable since this depends only on the ground state wavefunctions. The changes resulting from configuration interaction are very minor, no more than a few tenths of a ppm in σ^d, over the Hartree–Fock value. Where *ab initio* calculations are not available, it is possible to estimate σ^d to within 1 to 2 ppm even without wave functions. Flygare and co-workers have proposed an easy method of evaluating σ^d which has been shown to be reliable in evaluating the average and the components of σ from the spin rotation con-

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stants.[5,6] The success of this method is due to the fact that most of σ^d is given by the diamagnetic shielding of the free atoms and the rest can then be approximately calculated by the method of atomic dipoles.[7]

Experimental values of spin rotation constants are available from molecular beam magnetic and electric resonance experiments and also from high-resolution microwave spectroscopy. In the first two types of experiments the radiofrequency spectrum corresponding to the reorientation of the ^{15}N nuclear moment in a magnetic field, or the interaction of the electric dipole moment of the molecule with a strong external electric field, is composed of transitions from many J and M_J states which may be individually resolved.[8] In the third type of experiment, a specific purely rotational transition is observed. Vibrationally averaged constants are obtained, usually for the ground vibrational state, occasionally for a vibrationally excited state as well.[8] The relation between σ^p and M shown in Eq. (1) holds for a vibrationless molecule at the equilibrium nuclear configuration. Experimentally one usually obtains $\langle M_{\alpha\alpha}\rangle_{v=0}$ components of the vibrationally averaged spin rotation constant. For vibrationally averaged quantities, Eq. (1) becomes[9]:

$$\begin{aligned}\langle\sigma^N\rangle_{v=0} = (e^2/3mc^2)\Big\{\langle\Psi^0 \,|\, \textstyle\sum 1/r_i \,|\, \Psi^0\rangle_{v=0} \\ - \displaystyle\sum_{N'}{}' \langle Z_{N'}/r_{N'}\rangle_{v=0}\Big\} + (m_p/6mg_N) \\ \times \sum_{\alpha} \langle (M_{\alpha\alpha}^{(N)} - M_{\alpha\alpha}^{\mathrm{acc}})/G_{\alpha\alpha}^{(e)}\rangle_{v=0}\,. \qquad (3)\end{aligned}$$

The vibrational average in the third term in Eq. (3) is usually replaced by a ratio of vibrational averages, $\langle M_{\alpha\alpha}^{(N)}\rangle_{v=0}/\langle G_{\alpha\alpha}^0\rangle_{v=0}$. $M_{\alpha\alpha}^{\mathrm{acc}}$ (a contribution to the spin rotation constant which arises when one considers the magnetic fields associated with motion of the nuclear charges) is generally smaller than the experimental error in $M_{\alpha\alpha}^{(N)}$ and can therefore be ignored.[10] However the difference between $\langle M_{\alpha\alpha}^{(N)}/G_{\alpha\alpha}^{(e)}\rangle_{v=0}$ and $\langle M_{\alpha\alpha}^{(N)}\rangle_{v=0}/\langle G_{\alpha\alpha}^0\rangle_{v=0}$ can be as much as 10% of σ^{SR} in molecules containing hydrogen.[10] Incomplete knowledge of the first and second derivatives of σ with nuclear configuration presently makes it impossible to correct for this error, as Hindermann and Cornwell had done for HF.[9] The thermal average of σ^p can be approximated by using the spin rotation constants for the ground vibrational state alone. However, when a low frequency vibration exists and the spin rotation constants for the first excited vibrational state are substantially different from that of the ground vibrational state (such as in NNO), a proper thermal average has to be carried out. There are also rotational (centrifugal distortion) corrections which have to be made.

Given the possible sources of errors which we have mentioned above, some discrepancies may be observed in comparing shielding values derived from spin rotation constants with differences in thermal averages of shielding observed in nuclear magnetic resonance spectroscopy in the zero-pressure limit. However, the precision of most available spin rotation constants is still such that the sources of errors discussed above are not limiting. Thus, the absolute shielding values derived from spin rotation constants of nitrogen in several molecules do not include vibrational or rotational corrections. The nuclear configurations used in σ^{nuc} and σ^d are generally the equilibrium configuration. The σ^d values are from *ab initio* calculations where available, and others are approximate values calculated using the Gierke and Flygare method.[6] A summary of the available spin-rotation-derived nitrogen shielding values is shown in Table I. Some *ab initio* values for σ_e are also included where available.

As noted in Table I, the spin rotation constants for the ground vibrational state are usually the only ones which have been measured. A comparison of the thermal average shielding at room temperature with the spin-rotation-derived shielding for the ground vibrational state is generally well justified when the fractional populations of the vibrational excited states are small. In the case of NNO, the spin rotation constants have been measured for both the ground vibrational state (000) and the first excited state (01^10).[8] An estimate of the thermal average of σ in NNO can be made by assuming that only these levels exist, the excited state being doubly degenerate:

$$\langle\sigma\rangle^T \simeq [\sigma_{(000)} + \sigma_{(010)}\, 2e^{-h\nu_2/kT}]/[1 + 2e^{-h\nu_2/kT}]\,, \qquad (4)$$

where ν_2 for ^{14}N^{14}N^{16}O = 596.5 cm^{-1}.[11] This estimate is shown in Table I for 200, 300, and 400 K. We see that within the errors quoted for the (000) and the (01^10) values, the thermal average at room temperature of the absolute shielding is indistinguishable from the value for the ground vibrational state. However, the temperature dependence of σ may be compared with the experimentally observed temperature dependence of ^{15}N shielding in the zero-pressure limit.[12]

EXPERIMENTAL

Because of the lower sensitivity of the ^{15}N nucleus compared to the ^{19}F nucleus, these measurements are more difficult to obtain with comparable precision, even with the 99 at.% ^{15}N enriched gases that we used. With the larger number of FID's required to definitely locate the signal, and the longer periods between pulses, there is an accompanying lower precision due to spectrometer instabilities during data acquisition. In addition, the lower resonance frequencies translate into larger relative errors in the shielding. The work on the ^{19}F shielding scale described in the previous paper[2] also served as a practice run for the more challenging ^{15}N measurements. The special precautions taken to minimize systematic and random errors were described in the earlier paper.[2] Only the conditions and parameters specific to the ^{15}N nucleus are discussed below.

A sealed sample of anhydrous liquid ammonia was used to periodically check spectrometer reproducibility between samples since it requires the least effort. The temperature was regulated at 300 K with a constant correction of +0.3 K. Thus, the data reported here are at 300.3 K. Sweep widths of 1000 and 2000 Hz were used. Pulse width was 8 μs and optimum pulse repetition

TABLE I. Nuclear magnetic shielding from spin rotation constants for the ground vibrational state (except where indicated otherwise).

Nucleus	$C_{\parallel}=M_{zz}$ (kHz)	$C_{\perp}=\frac{1}{2}(M_{xx}+M_{yy})$ (kHz)	σ^{SR} (ppm)	σ^{nuc} (ppm)	σ^{p} (ppm)	σ^{d} (ppm)	σ (ppm)
$^{14}NH_3$[a]	6.695 ± 0.005[b]	6.764 ± 0.005[b]	−61.89 ± 0.05[b]	−28.17	−90.06[b]	354.56[c,d]	264.54 ± 0.05[b]
	6.71 ± 0.02[e]	6.77 ± 0.02[e]			−91[f]	360[f]	269[f]
	6.66 ± 0.2[g]	6.66 ± 0.2[g]			−88.17[h]	354.08[h]	265.9[h]
(theor. σ_e)							267.8[i]
$^{14}N^{14}N^{16}O$		2.35 ± 0.20[j]	−284 ± 24	−90.7	−374 ± 24[j]	416	42 ± 24[j]
		1.829 ± 0.065[k]	−221 ± 12	−90.8[k]	−312 ± 12[k]		105 ± 12[v]
(01^10)	0.124 ± 0.07[k]	1.904 ± 0.015[k]	−230[u] ± 2				96 ± 2[v]
200 K							104.26[w]
300 K							103.58[w]
400 K							102.79[w]
$^{14}N^{14}N^{16}O$		2.90 ± 0.26[j]	−350 ± 31	−121.7[j]	−471 ± 31[j]	442	−24 ± 31[j]
		3.06 ± 0.12[k]	−369 ± 15	−122.0[k]	−492 ± 15[k]		−44 ± 15[v]
(01^10)	3.80 ± 0.1[k]	2.60 ± 0.02[k]	−314[u] ± 2.5				12 ± 2.5[v]
200 K							−42.03[w]
300 K							−37.85[w]
400 K							−33.07[w]
$H^{12}C^{14}N$		10.4 ± 0.3[l]	−356 ± 10	−53.0	−408.98 ± 10[m]	377.62[n]	−31.4 ± 10[m]
		10 ± 4[o]			−418[f]	381[f]	−37[f]
(theor. σ_e)							−40.6[i]
$^{35}Cl^{12}C^{14}N$		2.5 ± 0.8[p]	−634 ± 205	−106	−740 ± 205[f]	434	−306 ± 205[f]
$^{15}N_2$		22.0 ± 1.0[q]	−425 ± 20	−60	−485.8 ± 20[h]	384.5[s]	−101.3 ± 25[r]
					−486[f]	384[f,x]	−102[f]
(theor σ_0)							−23.18[t]

[a] Spin rotation data on $^{15}NH_3$ are also available but these are less precise. See S. G. Kukolich, Phys. Rev. 172, 59 (1968).

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[t] E. A. Laws, R. M. Stevens, and W. N. Lipscomb, J. Chem. Phys. 54, 4269 (1971).

[u] Using $B_v = 12\,578.4978\ \mathrm{cm}^{-1}$ from R. Pearson, T. Sullivan, and L. Frenkel, J. Mol. Spectrosc. 34, 440 (1970). $\sigma_{\parallel}^{SR}$ neglected.

[v] Calculated using Flygare and Goodisman's method.

[w] Estimated thermal average (see text).

[x] This compares favorably with the best available value of 384.47 ppm from configuration interaction (CI) calculations by R. D. Amos, Mol. Phys. 39, 1 (1980).

[y] Spin rotation constants are also available for $CH_3{}^{14}NC$ [S. G. Kukolich, J. Chem. Phys. 57, 869 (1972)] and $P^{14}N$ [J. Raymonda and W. Klemperer, J. Chem. Phys. 55, 232 (1971)].

time was 0.55 s. 2 K data points were taken, zero-filling to 8 K. The number of scans varied from 200 to 4 K depending on the sample, although overnight acquisitions at various repetition rates were used as checks. Line widths varied from 0.4 to 2.6 Hz depending on the sample.

RESULTS

The resonance frequency for the bare nucleus could not be determined at this time since the ^{15}N absolute shielding scale is not as well defined as the ^{19}F absolute shielding scale. The corrections carried out for HF by

TABLE II. ^{15}N shielding differences between the isolated molecules at 300 K.[d]

			$\sigma_0^A(T)-\sigma_0^A(300\text{ K})=a_1(T-300)+a_2(T-300)^2+a_3(T-300)^3$		
A	$\dfrac{[\sigma_0^A(300\text{ K})-\sigma_0^{N_2}(300\text{ K})]}{[1-\sigma_0^{N_2}(300\text{ K})]}$	T (K)	10^3a_1	10^5a_2	10^7a_3
N_2	0 ± 0.02	220–360[a]	-1.11 ± 0.10	...	...
$\underline{N}NO$	$+161.08\pm0.02$	260–380[b]	-8.8816	-1.4682	$+1.9513$
$N\underline{N}O$	$+72.89\pm0.02$	260–380[b]	-3.5881	$+0.4102$	$+0.2009$
NH_3	$+326.16\pm0.06$	300–350[c]	$+6.55\pm0.82$	...	...
HCN	$+41.26\pm0.1$[e]				

[a] Reference 14.

[b] Reference 12.

[c] Reference 22.

[d] The value for CH_3NO_2, for comparison with other liquid phase data, is

$$\frac{[\sigma(\text{liq, 300 K, cyl, }\perp)-\sigma_0^{N_2}(300\text{ K})]}{[1-\sigma_0^{N_2}(300\text{ K})]}=-74.70\pm0.05\text{ ppm.}$$

[e] Calculated from measurements on the vapor in equilibrium with liquid HCN. Vapor frequencies observed at 365, 355, and 345 K were plotted as a function of vapor density (up to 6 amagats) and extrapolated to 300 K (0.95 amagat). Error estimate includes $\sigma_1\rho$.

Hindermann and Cornwell[9] to establish the ^{19}F absolute shielding scale can be carried out for N_2 since the first and second derivatives of σ with internuclear separation have been calculated by Laws *et al.*[13] and their first derivative agrees reasonably well with the measured temperature dependence of ^{15}N resonance in N_2 at the zero-pressure limit.[14] However, the spin rotation constant for N_2 is not yet precisely known, the error estimate being ± 20 ppm. Thus, we report our results in Table II as $[\sigma_0(300\text{ K})-\sigma_0^{N_2}(300\text{ K})]/[1-\sigma_0^{N_2}(300\text{ K})]$, since we divided frequency differences by the resonance frequency of ^{15}N in N_2 in the zero pressure limit, rather than the resonance frequency of the bare ^{15}N nucleus. We have included a liquid reference (CH_3NO_2) so that work in other laboratories may be related to our data. Neat liquid CH_3NO_2 has been recommended as the most suitable practical reference for nitrogen NMR.[15,16]

If we *assume* the absolute σ_0 of ^{15}N in NH_3 to be that obtained from what we believe to be the most accurate spin rotation constants and *ab initio* calculations, 264.54 ppm,[17] and use our shielding differences from Table II, we can calculate σ_0, the thermal average of shielding for ^{15}N in these isolated molecules. Each of these numbers will be shifted by a constant amount if the absolute shielding value for NH_3 is changed. In Table III we compare these values with σ_0 derived from spin rotation constants.

DISCUSSION

Comparison of σ_0 from gas phase NMR to that derived from spin rotation constants

In principle the ^{15}N shielding scale should be slightly different from the ^{14}N shielding scale due to the primary isotope shift for all the molecules and the secondary isotope shift in the multiple ^{15}N-labeled ones such as NNO and N_2. However, we will ignore isotope effects on σ in directly comparing our ^{15}N NMR results with spin-rotation-derived shielding for ^{14}N as well as with reported ^{14}N and ^{15}N chemical shifts in the liquid phase, since the isotope effects should be small compared to the quoted errors in these.[18]

We find discrepancies between our isolated molecule shielding values and the spin-rotation-derived values (Table III). The spin rotation data for N_2 and the central N atom in NNO are in disagreement with our results by 40 and 60 ppm respectively. These differences are well outside the error limits quoted for the spin rotation results. The other systems (HCN and $\underline{N}NO$) are in good agreement.

Some possible reasons for the discrepancies are the following: (a) Our values in Table III are based on the absolute σ_0 for NH_3 being defined as 264.54 ppm.[17] If the spin-rotation-derived value for NH_3 is in error, there will be apparent discrepancies. (b) The diamagnetic terms used in calculating the shielding values from spin rotation constants may be in error, in particular, the atom–dipole method used for the calculation of σ^d in NNO and HCN may be suspect. (c) The use of an improper vibrational average in Eq. (3) may be responsible. (d) The errors associated with the measured spin rotation constants may be underestimated.

First of all, we can eliminate (a). The largest discrepancy in Table III is in the internal chemical shift

TABLE III. Comparison of ^{15}N and ^{14}N absolute shielding (σ_0) derived from spin rotation constants with absolute σ_0 obtained from this study *assuming* $\sigma_0^{NH_3}$ (300 K) = 264.54 ppm.[17]

Nucleus	σ_0 (300 K), this study	σ_0 derived from spin rotation[a]
N_2	-61.6 ppm	-101.3 ± 20 ppm
$\underline{N}NO$	99.5	105 ± 12
$N\underline{N}O$	11.3	-44 ± 15
NH_3	(264.54)	264.54 ± 0.2
HCN	-20.4	-31.36 ± 10

[a] References are given in Table I, in which see other reported values also.

TABLE IV. Comparison of σ^{SR} for ^{15}N in various molecules with $(\sigma_0 - \sigma^d_{\text{free atom}})$. The free atom diamagnetic shielding is 325.5 ppm for ^{15}N.[a]

	σ^{SR} (ppm)[b]	$(\sigma_0 - 325.5)$ (ppm)
N_2	-425 ± 20	-387.2
$\underline{\mathrm{N}}\mathrm{NO}$	-221 ± 12	-226.1
$\mathrm{N}\underline{\mathrm{N}}\mathrm{O}$	-369 ± 15	-314.3
NH_3	-61.89 ± 0.05	-61.0
HCN	-356 ± 10	-345.9

[a] G. Malli and C. Froese, Int. J. Quantum Chem. Symp. 1, 95 (1967).

[b] See references in Table I.

between the two nitrogen nuclei in NNO. This does not depend on the choice of NH_3 as the standard.

Reason (b) was raised by Wrackmeyer as the possible reason for the discrepancy in comparisons with liquid phase chemical shifts. The diamagnetic term used for N_2 was taken from an *ab initio* calculation and is probably good to a tenth of a ppm. For this and for other molecules for which accurate calculations of σ^d have been carried out, it has been found that the method of Flygare and co-workers is accurate to within 1–2 ppm.[6] Let us consider this method briefly.

By formally partitioning the sum of $1/r_j$ over all j electrons into two sums, one over electrons "on" nucleus N and the other over all electrons "on" all the other nuclei, N', Flygare and co-workers[5,6] have been able to write the average diamagnetic shielding in terms of a free atom term, a contribution of the electronic point charges centered at the other nuclei, and a third term which arises if the point charges are not centered on the N' nucleus but are displaced by a distance $\langle \rho \rangle_{N'}$[7]:

$$\sigma^d_{\text{av}}(N) = \sigma^d_{\text{atom}}(N) + (e^2/3mc^2) \sum_{N'}{}' Z_{N'}/r_{N'} - (e^2/3mc^2) \sum_{N'}{}' \mathbf{r}_{N'} \cdot \langle \rho \rangle_{N'}/r^3_{N'} . \tag{5}$$

The second term in the above equation is identical in form and opposite in sign to σ^{nuc} which arises in writing the average paramagentic shielding term in terms of the spin rotation constants:

$$\sigma^p_{\text{av}}(N) = \sigma^{SR} + \sigma^{\text{nuc}} . \tag{6}$$

Thus, $\sigma(N)$ can be written in the Flygare method, as

$$\sigma_{\text{av}}(N) = \sigma^d_{\text{atom}}(N) + \sigma^{SR} - (e^2/3mc^2) \sum_{N'}{}' \mathbf{r}_{N'} \cdot \langle \rho \rangle_{N'}/r^3_{N'} . \tag{7}$$

This applies to the equilibrium configuration, with extension to thermal averages requiring some corrections which may be a few ppm. The last term is in general quite small (on the order of a few parts per million) relative to the preceding terms. Thus, $(\sigma_{\text{av}} - \sigma^{SR})$ for ^{19}F shielding has been found to be roughly constant and nearly equal to the free atom diamagnetic shielding.[10] If the third term in Eq. (7) is fairly small, then $(\sigma_0 - \sigma^d_{\text{atom}})$ should be quite close to the observed value of σ^{SR}. We compare them in Table IV and note that the agreement is good except for N_2 and $\mathrm{N}\underline{\mathrm{N}}\mathrm{O}$, the same chemical environments for which there is poor agreement between our measured σ_0 and the spin-rotation-derived shielding. It is interesting to note that the value of σ^{SR} reported for the (01^10) vibrational state is nearly the same as the $(\sigma_0 - \sigma^d_{\text{atom}})$ for $\mathrm{N}\underline{\mathrm{N}}\mathrm{O}$ in Table IV. A value of σ^{SR} closer to $(\sigma_0 - \sigma^d_{\text{atom}})$ for the ground vibrational state of $\mathrm{N}\underline{\mathrm{N}}\mathrm{O}$ would bring the spin-rotation-derived internal chemical shift closer to the observed value. This does not settle the question of which one is in error, the spin rotation constants or the atom–dipole method of estimating σ^d. In the case of N_2, the adequacy of the atom–dipole approximation has been demonstrated, the results are very close to the *ab initio* values.[6]

Wofsy *et al.*[10] have pointed out possible errors in using the ratio of a vibrationally averaged spin rotation constant to a vibrationally averaged rotational constant in Eq. (3). For N_2, this is not a likely source of difficulty. It has already been shown that the room temperature σ_0 of N_2 has a very small centrifugal distortion correction and a negligible vibrational correction,[14] i.e., σ_0(300 K) is very close to σ_0(0 K) or $\langle \sigma \rangle_{v=0}$. Thus, it is not likely that the discrepancy between using $\langle M^{(N)}_{\alpha\alpha} \rangle_{v=0}/\langle G^0_{\alpha\alpha} \rangle_{v=0}$, instead of taking the average, $\langle M^{(N)}_{\alpha\alpha} - M^{\text{acc}}_{\alpha\alpha})/G^{(e)}_{\alpha\alpha} \rangle_{v=0}$ is as large as 20 ppm. We conclude then that the error in the experimental spin rotation constant for N_2 must be somewhat larger than originally estimated. The vibrational correction for NNO is more difficult to assess since there are several vibrational modes and the two N nuclei will have differing vibrational corrections. Although an improper vibrational average has been used in taking $\langle M_{\alpha\alpha} \rangle_{v=0}/\langle G_{\alpha\alpha} \rangle_{v=0}$ rather than $\langle M_{\alpha\alpha}/G_{\alpha\alpha} \rangle_{v=0}$, it is unlikely that this difference, together with the centrifugal distortion contributions to σ_0 can be as large as 60 ppm. In contrast, of the eight molecules for which such comparisons as shown in Table III could be made in ^{19}F shielding, the largest difference found was 8 ppm.[2]

Let us consider the consistency of the spin rotation results with other experimental data. The spin rotation constants for the (000) state, obtained by Reinartz *et al.*,[8] gives an internal chemical shift in NNO which is 60 ppm too large, well outside of their quoted experimental errors. Since the constants for the (01^10) state give an internal chemical shift which is about right, the spin rotation constant for the central N nucleus in the NNO ground state appears suspicious.

The temperature dependence of $\sigma_0^{\underline{\mathrm{N}}\mathrm{NO}}$ and $\sigma_0^{\mathrm{N}\underline{\mathrm{N}}\mathrm{O}}$ have been reported[12] and may be compared with the estimated thermal average of the spin-rotation-derived shielding values shown in Table I. Fitted to a straight line, the latter give $d\sigma_0^{\underline{\mathrm{N}}\mathrm{NO}}/dT \simeq -0.007$ ppm/deg, which is identical to that obtained if the observed zero-pressure limit frequencies[12] are likewise fitted to a straight line. On the other hand, the same procedure yields $d\sigma_0^{\mathrm{N}\underline{\mathrm{N}}\mathrm{O}}/dT \simeq +0.045$ ppm/deg from Table I. which is about a factor of 10 too large and opposite in sign to the observed

TABLE V. Corrections which relate isolated molecule data to reported shifts in the liquid, all in ppm.

A	T_1	T_2	σ_0 (300 K)	$(d\sigma_0/dT) \times (T_2 - T_1)$	$\sigma_1\ (T_1)\ \rho$	Gas-to-liquid shift[f] at T_1	σ (liq, T_1)[g]
NH_3	300 K	300 K	264.54		-0.44[a]	-19.47[a]	244.6
N_2	77	300	-61.6	-0.25[b]	-0.017[b]	$\simeq -2.7$[c]	$\simeq -64.9$
$\underline{N}NO$	193	300	99.5	-0.75[d]	-0.019[d]	$\simeq -10.0$[c]	$\simeq 88.6$
$N\underline{N}O$	193	300	11.3	-0.36[d]	-0.008[d]	$\simeq -4.0$[c]	$\simeq 6.8$
HCN	300	300	-20.4			$\simeq +12.0$[e]	-8.32

[a] Reference 22.

[b] Reference 14.

[c] Estimated from $\sigma_1\ (T_1)\ (\rho_{liq} - \rho_{vap})$, using $\sigma_1\ (T)$ from Refs. 12 and 14 and liquid vapor equilibrium data from Landolt–Bornstein, *Zahlenwerte und Funktionen* (Springer, Berlin, 1966), IV Band, 4 Teil, Subteil a.

[d] Reference 12.

[e] Estimated from liquid observed at 300 K and equilibrium vapor observed at 365, 355, and 345 K extrapolated to 300 K.

[f] $[\sigma(\text{liq}, T_1) - \sigma(\text{equil vap}, T_1)]$.

[g] $\sigma(\text{liq}, T_1) = \sigma_0\ (T_2) + (d\sigma_0/dT)\ (T_2 - T_1) + \sigma_1\ (T_1)\ \rho\ (\text{equil vap}) + [\sigma(\text{liq}, T_1) - \sigma(\text{equil vap}, T_1)]$.

[h] References given in Table III.

$d\sigma_0^{N\underline{N}O}/dT$ in the zero-pressure limit.[12] This and the incorrect prediction of the internal ^{15}N chemical shift in $^{15}N^{15}NO$ casts doubt on the spin rotation derived value for the central nitrogen in NNO. Using Eq. (4) we find that a value of 15 ppm (instead of -44) for $\sigma_{(000)}^{N\underline{N}O}$ will reproduce the experimentally observed temperature dependence in the isolated molecule as well as the correct internal chemical shift. A value of 15 ppm for the (000) state is also more plausible than a value of -44 ppm when compared to 12 ppm for the (01^10) state.

There is additional evidence that the spin rotation constants for N_2 and $N\underline{N}O$ may be outside the quoted experimental errors. For linear molecules, the absolute shielding can be calculated from the experimental shielding anisotropy if $\sigma_{\parallel}^d$ can be estimated. This calculation depends on $\sigma_{\parallel}^p$ being zero for linear systems:

$$\sigma_{\parallel} = \sigma_{\parallel}^d ,$$

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} ,$$

$$\sigma_{av} = (\sigma_{\parallel} + 2\sigma_{\perp})/3 = (3\sigma_{\parallel}^d - 2\Delta\sigma)/3 . \tag{8}$$

For N_2, $\Delta\sigma$ has been measured by Ishol and Scott in the pure solid,[19] and reported as 603 ± 28 ppm. With the value of $\sigma_{\parallel}^d = 338.3$ from Laws *et al.*,[13] we get σ_{av} for $N_2 = -63.7 \pm 28$ ppm. There is undoubtedly a change in $\Delta\sigma$ in going from isolated molecule to solid phase. However, this change in $\Delta\sigma$ is expected to be no worse than about 5 ppm.[14] Given this *caveat*, the absolute σ calculated from the measured shielding anisotropy (-63.7) agrees with our value for σ_0(-61.6 ppm) much better than the spin-rotation-derived value of -101.3 ± 20 ppm.[19]

Similarly, $\Delta\sigma$ has been measured by Bhattacharyya and Dailey for both nitrogen nuclei in NNO.[20] They also calculated $\sigma_{\parallel}^d$ using Flygare's atom–dipole model. For $\underline{N}NO$, $\Delta\sigma = 366 \pm 10$ ppm and $\sigma_{\parallel}^d = 349$ ppm, Eq. (8) leads to $\sigma^{\underline{N}NO} = 105 \pm 10$ ppm. On the other hand, for NNO, $\Delta\sigma = 505 \pm 10$ ppm and $\sigma_{\parallel}^d = 364$ ppm, leading to $\sigma^{N\underline{N}O} = 27.3 \pm 10$ ppm. Their alternative set of $\Delta\sigma$ values, 369 ± 15 and 512 ± 10 ppm respectively yield $\sigma^{\underline{N}NO} = 103 \pm 15$ and $\sigma^{N\underline{N}O} = 22.7 \pm 10$ ppm. Here again, there is a medium shift in $\Delta\sigma$, which could be larger than 5 ppm for the end nitrogen. (It is known that the medium shift for the end ^{15}N in $\underline{N}NO$ is much larger than that for the middle ^{15}N nucleus.[12]) These values are in good agreement with our 99.5 and 11.3 ppm values. We note that all the experimental values for the end nitrogen in NNO agree remarkably well. In the case of the middle nitrogen (for which the medium effect is even smaller[12]), the ground vibrational state (000) has a spin-rotation-derived value which is in disagreement with (1) the measured internal chemical shift in isolated NNO molecule, (2) the temperature dependence of $N\underline{N}O$ shielding and (3) the shielding anisotropy of $N\underline{N}O$. We conclude that the spin rotation constant reported for the middle nitrogen nucleus in the ground vibrational state of NNO[8] may be in error.

Comparison of σ_0 values from gas phase NMR with liquid phase data

We calculated the magnitudes of the corrections linking the isolated molecule shielding to the shielding in the liquid phase. It should be noted that for ^{15}N shielding, these corrections are not small and vary substantially from one molecule to another. The liquid phase shielding values expected from applying these corrections to the σ_0 obtained in this study are shown in Table V. The ^{15}N gas to liquid shifts are very sensitive to temperature, can be rather large,[22] and unlike ^{19}F gas to liquid shifts, vary greatly from molecule to molecule.[23] Thus, we see in Table V the ^{15}N shielding difference between liquid NH_3 and liquid HCN differs from the shielding difference between an isolated NH_3 molecule and an isolated HCN molecule by 31.5 ppm at 300 K. Under such circumstances, it is not surprising that the NH_3–HCN chemical shift in the liquid phase does not agree with the difference in spin-rotation-derived shielding.[1]

TABLE VI. Estimates of absolute shielding for ^{15}N nuclei in condensed phases, from reported chemical shifts.

	$^{15}N\ (\sigma-\sigma_{ref})/(1-\sigma_{ref})$, ppm										Combined	
System	c	d	e	f	g	h	i	j	k	l	$(\sigma-\sigma_{ref})^a$	Absolute^b σ
CH_3NO_2 (liq, 298 to 303 K)	0 (303 K)					0 (300 K)	0 (303 K)		0 (298 K)		0	−135.8
NO_3^- (satd NH_4NO_3)		0			0		3.98				3.98 (i)	−131.8
NO_3^- (5*M* NH_4NO_3, 2*M* HNO_3)				0			4.64				4.64 (i)	−131.2
NO_3^- (7*M* HNO_3)			0				12.59				12.59 (i)	−12.3
N_2 (liq, 77 K)		70		65.6							74 (d) 70.2 (f)	−61.8 −65.6
N_2 (gas, 303 K)	75.3										75.3 (c)	−60.5
HCN (liq, 309 K)					125						129 (g)	−6.8
HCN (liq, 300 K)						128.0					127.5 (h)	−8.3
CH_3CN (equil vap, 227.5 K)								−273.4			126.7 (j)	−9.1
CH_3CN (liq, 303 K)							136.40	−263.7			136.40 (i)	+0.6
CH_3CN (liq, 227.5 K)								−262.1			138.0 (j)	+2.2
ClCN (liq, 309 K)					140						144 (g)	+8.2
$N\underline{N}O$ (liq, 193 K)		138									142 (d)	+6.2
$N\underline{N}O$ (CCl_4, 303 K)			135.40								148.0 (e)	+12.2
$\underline{N}NO$ (liq, 193 K)		222									226 (d)	+90.2
$\underline{N}NO$ (CCl_4, 303 K)			219.66								232.3 (e)	+96.5
NH_4^+ (satd NH_4NO_3)							359.55				359.55 (i)	+223.8
NH_3 (liq, 195.5 K)								−22.6			377.5 (j)	+241.7
NH_3 (liq, 298 to 303 K)						380.9 (300 K)	381.93 (303 K)	−18.0 (303 K)	380.23 (298 K)	0 (302 K)	380.23 (k) 380.4 (h) 381.93 (i) 382.1 (j)	244.4 244.6 246.3 246.1
NH_3 (equil vap, 302 K)										17.2	399.3 (l)	263.5
NH_3 (equil vap, 195.5 K)								0			400.1 (j)	264.3

[a] For all except our values $(1-\sigma_{ref})$ was taken to be 1. No attempt has been made to correct for volume susceptibility.

[b] Based on $\sigma^{CH_3NO_2}$ (neat liquid, 300 K) = −135.8 ppm, obtained by assuming $\sigma_0^{NH_3}$ (300 K) = 264.54 ppm.

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Assignments of absolute shielding in condensed phases based on ^{15}N chemical shifts measured in liquids or solutions in various laboratories are not unique, since several reference systems have been used for ^{15}N. This is not a problem in itself, since one can measure the ^{15}N chemical shifts of various reference systems relative to any chosen one.[15,16] The problem is that the exact composition of the reference systems used were not always specified. For purposes of comparison with our isolated molecule shielding values (σ_0), we have compiled the reported shifts of the compounds studied here and the respective reference systems used. From our measured shielding for CH_3NO_2 liquid at 300 K (in a cylindrical sample with axis perpendicular to the magnetic field), -74.70 ± 0.05 ppm relative to isolated N_2 molecule, and an assumed absolute $\sigma_0^{NH_3}$ (300 K) = 264.54 ppm, we compute an absolute σ for ^{15}N in liquid CH_3NO_2 under these conditions, -135.8 ppm. It is this value that we use to convert reported chemical shifts to absolute σ in Table VI. Of course these numbers will all change by a constant amount if the absolute σ_0 for ^{15}N in NH_3 is found to be different. There are unknown errors associated with most reported chemical shifts, and the numbers in Table VI are probably not immune to such errors. Nevertheless, the internal consistency in the combined data in Table VI is probably not worse than ± 2 ppm.

CONCLUSIONS

We find that the corrections which have to be made in ^{15}N shielding (in contrast to ^{19}F shielding), in linking the isolated molecule data at 300 K to the liquid phase data at some other temperature, are sometimes sizeable (e.g., about -20 ppm for ^{15}N in NH_3) and of differing signs (e.g., about $+12$ ppm for ^{15}N in HCN). These alone account for the previously noted discrepancies between the spin-rotation-derived values of nuclear shielding and the liquid phase NMR values in NH_3 and HCN. We have also seen that large inconsistencies with other experimental data indicate that the spin rotation constant for the middle nitrogen in the ground vibrational state of NNO[8] may be in error, and that the error limits originally reported for the spin rotation constant of N_2[19] may be somewhat underestimated. With NMR measurements in the limit of zero pressure of shielding relative to an isolated N_2 molecule, we have provided a basis for an absolute nitrogen shielding scale. Vibrational corrections for N_2 of the same nature as has been done for HF[9] are possible, as soon as more reliable first and second derivatives of nuclear shielding with the internuclear distance in N_2 are available. Then, the values in Table II will provide an absolute nitrogen shielding scale which is as reliable as the fluorine shielding scale.

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