

Ammonia: the molecule for establishing ^{14}N and ^{15}N absolute shielding scales and a source of information on nuclear magnetic moments

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ABSTRACT

Multinuclear NMR studies of the gaseous mixtures $^3\text{He}/^{14}\text{NH}_3$ and $^3\text{He}/^{15}\text{NH}_3$ are reported. Precise analysis of the ^3He , ^{14}N , ^{15}N and ^1H resonance frequencies show linear dependence on the gas density. Extrapolation of these results to the zero-pressure limit gives $\nu_0(^1\text{H})$, $\nu_0(^{14}\text{N})$ and $\nu_0(^{15}\text{N})$ resonance frequencies of the isolated ammonia molecule at 300K. The analogous value for ^3He atoms in gaseous mixtures $\nu_0(^3\text{He})$ was measured as well. The application of a new scheme to introduce the most important electronic effects on NMR shieldings, together with highly accurate quantum chemical shielding calculations allow the $^{14/15}\text{N}$ and ^1H shielding of the isolated ammonia molecule to be obtained with the greatest accuracy and precision. For the first time, these studies were carried out on ammonia within the so-called four-component relativistic framework. The NMR frequency comparison method provides an approach for determining the ^{14}N and ^{15}N nuclear magnetic moments. The new shielding parameters in ammonia were used for reevaluation of the entire nitrogen absolute shielding scale. Additionally, the absolute shielding values of several gaseous compounds and secondary reference substances in liquids were presented. It was established that ^{14}N and ^{15}N absolute shielding constants in $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ are very similar, and only differ by less than 0.01 ppm, which is not usually measurable in NMR experiments. Precise calculations of ^{14}N and ^{15}N dipole moments were also made from these accurate shielding values.

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I. INTRODUCTION

It is very useful when one element possesses at least two magnetically active isotopic nuclei with different spectroscopic properties. Quite different resonances can be used and isotope effects examined. This is the case for the nitrogen atom, composed from two stable isotopes (^{14}N , 99.63%) and (^{15}N , 0.37%) with spin numbers 1 and $\frac{1}{2}$, respectively. Despite the high natural abundance, application of ^{14}N to many chemical substances was preferred in the first stages of NMR spectroscopy. Its experimental conditions are not very favourable due to a low gyromagnetic ratio and strong quadrupolar interactions ($Q=+0.02001(10)$ b). The measured resonance signals have a low observable resonance frequency and a rather large half-width ranging from a few Hz up to several kHz. Additional problems arise with possible baseline distortions caused by “acoustic ringing” of the probe. The resulting spectra have a poor signal-to-noise ratio (S/N) and require lengthy analysis. On the other hand, ^{15}N resonance yields sharp lines but is very insensitive. Fortunately, its signals can be detected by the ^1H - ^{15}N heteronuclear correlation technique as a more sensitive alternative in many circumstances. Inverse detection of ^{15}N signals can be altered as many as 9 times. ^{15}N isotopically-enriched compounds are useful to improve the sensitivity of analysis. A few chemical companies exist today that offer a number of nitrogenous compounds enriched with ^{15}N nuclei. Fortunately, heteronuclear correlation techniques belong to the more popular of those suitable for nitrogen macromolecules: amines, amides, amino acids, peptides, proteins and many others. The chemical shift values and spectral ranges (~ 900 ppm) are identical for both nitrogen isotopes.

It is very important to know the values of the absolute shielding of nitrogen compounds with the greatest accuracy. Besides the status of the nitrogen NMR among other resonances, the shielding constants for compounds of chemical, biological and medical importance can serve as good references for many quantum chemical calculations. The fundamental principle of absolute scale lies in taking shielding values against bare nuclei, without electrons, where 0.0 ppm of shielding is a starting point. Because measurements of bare nuclei are not possible in the NMR spectrometer, accurate data for the selected reference substance is strongly recommended. Measuring NMR chemical shifts in the gas phase is very

worthwhile, as accurate and precise theoretical calculations can then be made. The combination of these methods leads to the absolute shielding for a given nuclei in the selected molecule being established. Several NMR scales were settled successfully in this way: ^1H , ^{13}C , ^{17}O , ^{33}S , ^{31}P and some others.¹⁻³ Given the just mentioned difficulties for obtaining absolute NMR shieldings, several theoretical methods were developed to get them. One of the most accurate methods was recently published by Gauss and collaborators.³ They used the Ramsey-Flygare relationship among nuclear spin-rotation tensor (which are measured with high accuracy) and shieldings. This relationship is only valid within the non-relativistic, NR, framework so that they first obtained truly non-relativistic values for the experimentally measured spin-rotation constant at equilibrium geometry. Then the Ramsey-Flygare relationship was applied for getting the paramagnetic shielding constant and, afterwards, the NR diamagnetic contribution, zero-point vibrational corrections, ZPV, and temperature effects are introduced to obtain the semi-experimental absolute shielding constants of light-atoms like ^{17}O in H_2O and ^{33}S in H_2^{33}S .

Ammonia is a good example of prime reference in establishing the nitrogen absolute shielding scale. The shielding constants in a single ammonia molecule have been calculated several times in recent decades. Unfortunately, none of them take into account the relativistic effects. From previous investigations into ^{13}C (~1 ppm) and ^{17}O (2-3 ppm) shielding constants, it is known that these effects are necessary and cannot be omitted when high quality results are required. Relativistic effects were only recently involved in making theoretical calculations.⁴⁻¹⁰ We can expect that relativistic effects on ^{14}N and ^{15}N for ammonia will be around ~1.5 ppm and, in principle, these cannot be neglected. As one of the newest attempts to get the most reliable theoretical results for absolute NMR magnetic shielding constants of both, nitrogen and hydrogen nuclei in ammonia, we performed calculations involving electron correlation, relativistic corrections, zero-point vibration and temperature effects, all of them treated within a new theoretical scheme. We first considered the equilibrium experimental geometry of ammonia on top of which four-component relativistic effects were obtained, together with NR electron correlation, ZPV and temperature effects. The total theoretical value of absolute shieldings of nitrogen and hydrogen atoms in ammonia are also compared with highly accurate experimental measurements in order to check them both.

In this work, the NMR parameters for $^3\text{He}/^{14}\text{N}\text{H}_3$ were measured in the gas phase. ^1H and ^{14}N NMR frequencies in the ammonia molecule and ^3He in helium atoms were extrapolated to the zero-density limit and were then used to recalculate the ^{14}N nuclear

magnetic moment and NMR absolute shielding constant. Similar experimental results were published some time ago using the $^{15}\text{NH}_3$ form of the ammonia molecule.^{5,10} They are discussed in detail in this work.

II. EXPERIMENTAL

Small amounts of the ^3He ($<5\times 10^{-3}$ mol/L) in $^{14}\text{NH}_3$ as a buffer gas were placed in the glass ampoules. The total range densities were maintained in the range 0.04 – 0.5 mol/L. ^3He (99.9%, Eurisco-Top, France) and $^{14}\text{NH}_3$ (99.9%, Aldrich) were used from lecture bottles without further purification. $^{15}\text{NH}_3$ (99.8%) was obtained from Aldrich-Sigma and used for preparation of pure ammonia gaseous samples. They are without helium-3 additives but one sample with $^3\text{He}/\text{SF}_6$ of known chemical shift was interchangeably measured.

A fixed arrangement of gaseous samples was used: the inner 4mm o.d. glass tube with gas mixtures and the outer NMR tube 5mm o.d. (Wilmad, 552 PP) containing deuterated solvent for the lock system – cyclo- C_6D_{12} . All samples were prepared in a conventional glass vacuum line equipped with an oil Varian SD90 pump and liquid nitrogen cold traps as described earlier.¹¹

The ^1H , ^3He and $^{14/15}\text{N}$ NMR resonance frequencies were measured on a Varian-INOVA 500 MHz spectrometer operating at 500.607 MHz, 381.358, 36.175 MHz and 50.725 MHz, respectively. The standard two channel Varian LB (low band) 10 mm probe was used for ^1H and ^{14}N NMR signals and the Varian sw5 (switchable) 5 mm probe for ^1H and ^{15}N spectra. The ^3He spectra were acquired in the self-reconstructed helium probe¹². All ^1H and $^{14/15}\text{N}$ NMR chemical shifts were referenced according to the primary reference substances: external liquid TMS and liquid CH_3NO_2 . The $^2\text{H}(\text{D})$ NMR signals of lock substance $\text{c-C}_6\text{D}_{12}$ were measured in the lock channel of each probe sequentially after normal spectra measurements without the stabilisation process (lock). The gas phase results were presented as linear density functions. For the analytical solving these dependences we have used the linear regression method with errors in the frequency/shielding domain. The determination R^2 coefficients were cited in the Figures 1 and 2.

Additionally, several pure gas compounds were examined at different pressures: nitrous oxide (NNO), nitrogen trifluoride (NF_3) and nitrogen (N_2). The absolute shielding of nitrogen at 300K and their zero-pressure limit are also reported. The $^{14}\text{ND}_3/^{15}\text{NH}_3$ equimolar gas phase sample was prepared at total pressure of 7.05 atm and ^{15}N NMR spectrum was recorded.

III. THEORETICAL APPROACH

Concerning the theoretical models used to calculate the absolute shieldings of both, nitrogen and hydrogen atoms, we shall first express that we have considered different levels of theory with large enough basis sets, and London type orbitals. We have analysed the convergence of results with different kind of basis sets including the Dunning and Dyall basis. At the end we performed all calculations with the dyall.acv4z basis set.¹³ Within the non-relativistic [NR] framework we performed calculations at RPA [RPA-SOPPA], PBE0 [PBE0], and SOPPA [RPA-SOPPA] ;and SOPPA-CCSD [SOPPA-CCSD] levels of approach using the Dalton code.¹⁴ Within the four-component relativistic framework we also performed calculations at RPA and PBE0 levels of theory using the Dirac code.¹⁵

Relativistic effects for ¹⁴N and ¹⁵N isotopes were obtained as the difference between four-component RPA and NR-RPA calculations, both with London orbitals.¹⁶ On the other hand, the electron correlation effects were taken as the difference between NR-SOPPA-CCSD and NR-RPA calculations without London orbitals.¹⁷ In the case of ¹H the electron correlation contribution was taken as the difference between SOPPA and NR-RPA calculations.¹⁸ For the hydrogen atom, the SOPPA calculations are accurate enough.¹⁹

It is worth mentioning here that we assumed that relativistic effects can be considered as independent of the electron correlation effects. This is so because all atoms involved in our study are light-atoms. Correlation is then calculated within the NR regime using one of the most accurate methods we have at hand. Furthermore, in all cases the experimental geometry was considered in order to avoid geometric effects that could introduce differences with experimental measurements. ZPV corrections were included within the NR framework through calculations performed with the DALTON suite of programs at a temperature of 300 K.¹⁴ By using the appropriate keyword we calculated the harmonic contribution to the (ro)vibrational average to the nuclear shielding constants at 300K for ammonia.²⁰ It is important to realize that since each isotopic species for each temperature will have its own unique (ro)vibrationally averaged geometry, we have to calculate the harmonic contribution for each temperature and each isotopic species separately.

IV. RESULTS and DISCUSSION

A. Calculations of absolute shielding constants in the ammonia molecule

Theoretical calculations of shielding parameters in the isolated molecule play a crucial role in establishing the absolute shielding scale for any given nucleus. The ^1H and $^{14/15}\text{N}$ reference values should be calculated as accurately as possible. In this context, the hydride compounds are the best choice of subject because of their simplicity. The ammonia molecule was the subject of many theoretical investigations of shielding (screening) effects for years. The first calculations were made using Ramsey's general theory of magnetic shielding^{21,22} where the shielding was arbitrarily divided into two parts: diamagnetic, σ_d , and paramagnetic, σ_p . The first part depends on the ground-state wave functions as they are readily calculated with great accuracy. The paramagnetic term arises from the mixing of the ground state and different excited states. According to Flygare's method²³ the paramagnetic term can be obtained using the spin-rotation constants. Fortunately, spin-rotational (SR) constants C_p (in kHz) can be found from several experimental methods: (PAS) photo-association spectroscopy, (LIF) laser-induced fluorescence and (MW) microwave spectroscopy. This methodology was achieved by the first attempts to establish the absolute shielding scale of nitrogen nuclei. These kinds of scales can be seen as empirical or semi experimental because the spin-rotation constants were measured experimentally using the molecular-beam magnetic-resonance method or microwave spectra analyses.^{24,25} The Flygare's model as fully nonrelativistic is now outdated. In new relativistic approaches the division for dia and paramagnetic shielding parts is not much good. On the other hand, the purely theoretical calculations were performed by several *ab initio* methods. The evaluations involving different contributions of shielding are more valuable: equilibrium geometry, zero-point vibration corrections, temperature effects and electron correlation effects.²⁶⁻²⁹ Several of such selected results that were obtained by the most advanced methods are shown in Table 1.

Table 1. $^{14/15}\text{N}$ and ^1H shielding constants in the ammonia molecule.

$\sigma(^{14}\text{N}/^{15}\text{N})$	Method/Reference	$\sigma(^1\text{H})$
264.5(10)	from the spin-rotation constant in $^{14}\text{NH}_3$ [24]	31.2(10)
263.54(20)	redefined for gaseous ammonia measurements [25]	
269.7; 270.76	GIAO ansatz with CCSD and CCSD(T) method [26]	31.6
265.356	full triples corrections to vibrational averaged values at CCSD(T) level [27]	30.984
264.1; 263.9	CCSD/MP2 and CCSD(T) level of theory [28]	
263.83	CCSD(T) calculations with ZPV corrections [10]	30.94
266.217÷271.339	B3LYP, BHandH, CCSD(T) methods [29]	

266.7804	$^{14}\text{NH}_3$: theoretical calculations [This work]	31.3315
266.7878	$^{15}\text{NH}_3$: theoretical calculations [This work]	31.3327
266.54	$^{14}\text{NH}_3$: empirical calculation from Eq.(4) using ^1H and $^2\text{H(D)}$ lock data [This work]	30.726
266.58	$^{15}\text{NH}_3$: empirical calculation from Eq.(4) using ^1H and $^2\text{H(D)}$ lock data [This work]	30.735

Applying the methodology mentioned above, by which we introduce the most important effects in a very accurate way, we found that our best theoretical estimate for $\sigma(^{14}\text{N})$ in ammonia molecule is: 261.9553 (NR-RPA) + 6.0365 (electron correlation) + 1.6909 (relativistic) – 2.9023 (ZPV) = 266.7804 ppm, and for $\sigma(^1\text{H})$ is: 31.5988 – 0.0359 (relativistic effect) – 0.1184 (ZPV) = 31.3315 ppm.

In the same manner, our best estimates for $\sigma(^{15}\text{N})$ and $\sigma(^1\text{H})$ in $^{15}\text{NH}_3$ are 266.7878 ppm and 31.3327 ppm, respectively. All these results are shown in Table 1.

B. NMR shielding parameters from gas phase measurements

The main spectroscopic parameter measured in the one-dimensional spectrum is the chemical shift δ , defined as $10^6(v_{\text{sample}} - v_{\text{reference}})/v_{\text{reference}}$ and expressed in ppm. In the more fundamental description of magnetic properties, the nuclear magnetic shielding constant σ is preferred.³⁰ The relationship between these two parameters is approximately described as: $\delta = \sigma_{\text{ref}} - \sigma$, where σ is the shielding (screening) constant of the specific nucleus in the given molecule. Both values are specified in ppm (parts per million) but their magnitudes are of opposite signs. The nuclear shielding is a property that is distinguished as the screening effect on the nucleus by the surrounding electrons. These values are often affected by the intermolecular interactions, and are always present in liquids, liquid solutions and even in the gas phase. Only in this last case it is possible to avoid intermolecular interactions by the simple procedure of extrapolating the measured parameters to the zero-density (zero-pressure) limit and obtaining values for the so called “isolated” molecule at the temperature of the experiment.³¹ These kinds of results are relatively easy for theoreticians to accurately obtain in quantum-chemical calculations. The experimental NMR signal positions for each density/pressure series can be presented as chemical shifts, nuclear magnetic shielding values, or simply, resonance frequencies, as we achieved in this work.

Fig.1. shows the linear behavior of radio frequencies plotted against density and the extrapolated results $\nu_0(^1\text{H})$, $\nu_0(^{14}\text{N})$ and $\nu_0(^3\text{He})$ are available from the Eq.(1):

$$\nu(^1\text{H}, ^3\text{He}, ^{14}\text{N}) = \nu_0(^1\text{H}, ^3\text{He}, ^{14}\text{N}) + \nu_1(^1\text{H}, ^3\text{He}, ^{14}\text{N}) \rho(\text{NH}_3) \quad (1)$$

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where ρ is the density of the NH_3 as gaseous solvent expressed in mol/L units.

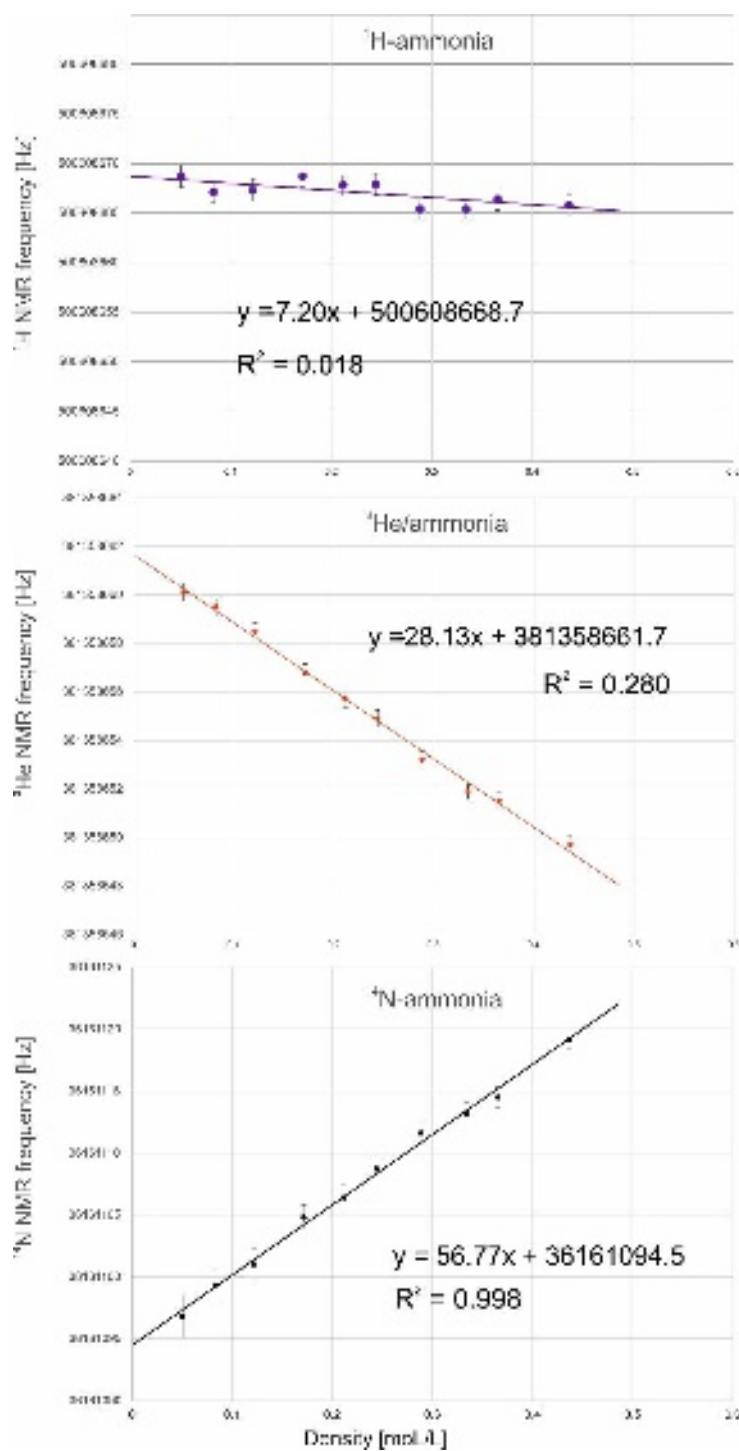


Figure 1. Density dependence of the ^1H , ^3He and ^{14}N resonance frequencies of $^3\text{He}/^{14}\text{N}$ gaseous mixtures at temperature 300K and magnetic field 11.75T.

Analogous linear functions can be written with respect to the shielding parameters as:

$$\sigma(^n\text{X}) = \sigma_0(^n\text{X}) + \sigma_1(^n\text{X})\rho(Y) \quad (2)$$

for ^nX nucleus present in any Y gaseous substance.

All appropriate NMR parameters from Eq.(1) were included in Table 2.

Table 2. ^1H , ^3He and $^{14/15}\text{N}$ NMR parameters: ν_0 [MHz], ν_1 [Hz mol $^{-1}$ L], σ_0 [ppm] and $\mu(\text{X})\mu_{\text{N}}$ measured and applied in the $^{15}\text{NH}_3$ and $^3\text{He}/^{14}\text{NH}_3$ gaseous systems.

System $^{14}\text{NH}_3/^3\text{He}$					
$\nu_0(^1\text{H})$	500.6086687(7)	$\sigma_0(^1\text{H})$	30.976	$\mu(^1\text{H})$	2.7928473446(8)
$\nu_1(^1\text{H})$	-7.2(28)				
$\nu_0(^{14}\text{N})$	36.1610948(17)	$\sigma_0(^{14}\text{N})$	266.791	$\mu(^{14}\text{N})$	0.40357368(7)
$\nu_1(^{14}\text{N})$	5.8(59)				
$\nu_0(^3\text{He})$	381.3586617(2)	$\sigma_0(^3\text{He})$	59.96703(2)	$\mu(^3\text{He})$	-2.12762531(3)
$\nu_1(^3\text{He})$	-28.1(5)				
$\nu(\text{lock})\text{C}_6\text{D}_{12}=76.846400(2)$; $\nu(\text{CH}_3\text{NO}_2)=36.1755188(1)$; $\nu(\text{TMS})=500.607623(1)$					
System $^{15}\text{NH}_3/^3\text{He}$					
$\nu_0(^1\text{H})$	500.608665(10)	$\sigma_0(^1\text{H})$	30.976	$\mu(^1\text{H})$	2.7928473446(8)
$\nu_1(^1\text{H})$	8.8(6)				
$\nu_0(^{15}\text{N})$	50.7252347(5)	$\sigma_0(^{15}\text{N})$	266.791	$\mu(^{15}\text{N})$	-0.28305791(3)
$\nu_1(^{15}\text{N})$	95.2(1)				
$\nu_0(^3\text{He}/\text{SF}_6)$	381.3586620(10)	$\sigma_0(^3\text{He})$	59.96703(2)	$\mu(^3\text{He})$	-2.12762531(3)
$\nu(\text{lock})\text{C}_6\text{D}_{12}=76.8464015$; $\nu(\text{CH}_3\text{NO}_2)=50.745464(1)$; $\nu(\text{TMS})=500.607623(1)$; $\nu(\text{C}_6\text{D}_{11}\text{H})=500.608190(1)$					

C. $^{14}\text{N}/^{15}\text{N}$ nuclear dipole moment

The NMR comparative method is crucial for determining nuclear magnetic dipole moments.¹⁰ The conventional relationship between two frequencies measured in one sample and the same B_0 magnetic field was used. In these experiments, the frequencies in the isolated molecule - ν_{N} , and ν_{H} for nitrogen and proton in NH_3 were applied:

$$\Delta\mu_{\text{N}}^z = \frac{\nu_{\text{N}}}{\nu_{\text{H,He}}} \cdot \frac{(1-\sigma_{\text{H,He}})}{(1-\sigma_{\text{N}})} \cdot \frac{I_{\text{N}}}{I_{\text{H,He}}} \Delta\mu_{\text{H,He}}^z \quad (3)$$

where related symbols have their usual meaning. For the helium reference, the $\nu(^3\text{He})$ frequency was used instead this of proton. $\Delta\mu_{\text{X}}^z$ is the z-component of the X magnetic moment; in the superconducting magnet of the NMR spectrometer measured in the z-direction of the magnetic field. The nuclear magnetic moment $\Delta\mu_{\text{X}}^z$, often described shortly as $\mu(^n\text{X})$ is quoted in nuclear magnetons n.m. ($\mu_{\text{N}}=5.050783699(31)10^{-27} \text{ JT}^{-1}$). We have assumed that

spin numbers and signs of nuclear moments for both nuclei are known. Our experimental frequency data was used to calculate $^{14/15}\text{N}$ nuclear magnetic moments. The reference nuclei are the ^1H and ^3He nuclides here. Fortunately, extremely accurate results of both magnetic moments have been established before. The first was directly measured in the double Penning trap experiment as $\mu(^1\text{H})=2.79284734462(82)\mu_{\text{N}}^{32}$ in nuclear magnetons. The second one is known from measurements of NMR spin precession frequencies of optically pumped low pressure ^3He and from protons in water. It is found that $\mu(^3\text{He})=-2.127625309(10)\mu_{\text{N}}^{33}$. when a recent highly accurate shielding correction $\sigma_0(^3\text{He})=59.967029(23)\text{ppm}^{34}$ is applied. New nitrogen nuclear magnetic moments were calculated taking into account these reference values - frequency ratios and shielding corrections - and all these values are shown in Table 2. They are as follows: $\mu(^{14}\text{N})=0.40357360(52)\mu_{\text{N}}$, $\mu(^{15}\text{N})=-0.28305788(36)\mu_{\text{N}}$ measured against the proton moment and $\mu(^{14}\text{N})=0.40357376(52)\mu_{\text{N}}$, $\mu(^{15}\text{N})=-0.28305794(36)\mu_{\text{N}}$ measured against helium-3. The results were finally averaged and included in Table 2. They will be used for verifying our theoretical calculations of shielding parameters in the ammonia molecule (see next section). The ratio of different nitrogen nuclear magnetic moments is then $\mu(^{14}\text{N})/\mu(^{15}\text{N})=-1.4257635$.

In general, the nuclear magnetic moments are vectors. In the uniform stable magnetic field only the one-dimension part, $\Delta\mu_X^z(^{14,15}\text{N})$, can be measured (as in Eq.(2)). It can always be recalculated to the full-length vector by applying the simple relation:

$\mu_X^{\text{length}} = \sqrt{I_X(I_X + 1)}/I_X \mu_X$ where I_X is the spin quantum number. Remember that the nuclear magnetic moment can be formulated in terms of the g_I factor $\Delta\mu_X^z/I_X$ or gyromagnetic ratio γ_X , which is the ratio between the magnetic dipole moment and its angular momentum:

$\mu_X = h/2\pi\gamma_X I_X$; g_I and γ_X are constants for each individual nuclide. They are:

$g(^{14}\text{N})=0.40357368$ and $g(^{15}\text{N})=-0.56611588$, $\gamma(^{14}\text{N})=1.93288244\times 10^7$,

$\gamma(^{15}\text{N})=-2.71136470\times 10^7(\text{JT}^{-1})$. Bear in mind that the negative sign of μ_X means that the magnetic moment as a vector is not aligned with the angular momentum, and positive signs means that it is aligned with the angular momentum for a given nuclei. In the case of nitrogen, it is definitely noticeable because both isotopes are distinguished by opposite signs of their dipole moments. There are small but clear differences between our new measured dipole moments and moments derived from older estimates.^{35,36} Nevertheless, these small discrepancies are of prime importance for the consistency of NMR parameters, as discussed below.

D. $^{14/15}\text{N}$ nuclear magnetic shielding of ammonia molecules

As it can be seen from Eq.(3) the nuclear magnetic shielding constant of ^1H or $^{14/15}\text{N}$ in the ammonia molecule can be determined in a semi-experimental way as:³⁷

$$\sigma_X = 1 - \frac{\nu_X}{\nu_D} \frac{|\mu_D|}{|\mu_X|} \frac{I_X}{I_D} (1 - \sigma_D) \quad (4)$$

where ν_X , μ_X and I_X mean the resonance frequencies, the nuclear magnetic moments and the spin numbers of $^{14/15}\text{N}$ or ^1H nuclei, observed in the experiment. The ν_D , μ_D and I_D belongs to the deuterium nuclei of the solvent used in the experiment. This relationship can serve as verification of quality for all parameters present in the above formula. It is clear that the precision and accuracy of dipole moments is crucial for solving the above equation. We have used the proton NMR signals of the residual peak of the lock substance (c- C_6HD_{11}) and the deuteron signal of c- C_6D_{12} with frequency 76.8464015 MHz. When the appropriate parameters from Table 1 are used, the calculated magnetic shielding constant in the ammonia molecule is $\sigma_0(^{14}\text{N})=266.54(7)$ ppm and $\sigma_0(^{15}\text{N})=266.58(7)$ ppm. If we used the data from the TMS signal ($\sigma(300\text{K})=32.815(5)$) ppm⁵ as a reference, more or less the same results would be achieved. Excellent agreement with the original calculated value 266.78 ppm is then stated. Analogous calculations of proton shielding constants using Eq.(4) gave $\sigma_0(^{14}\text{NH}_3)=30.726$ ppm and $\sigma_0(^{15}\text{NH}_3)=30.735$ ppm (see Table 1). All the received results are congruent to a high degree. Our newest shielding value in ammonia was used to recalculate the shieldings of several gas phase nitrogen containing molecules (see next section).

E. Nuclear magnetic shielding of nitrogen-containing compounds

The values of the nuclear magnetic shielding in simple nitrogen-containing molecules were previously measured in gas phase at the zero-pressure limit and collected by Jameson.^{25,38-41} Those results are then referenced against the new value of the shielding of ammonia and are given in Table 3. Most of these results were obtained from extrapolation of shielding values to the zero-pressure limit. Figure 2 shows the density dependences of ^{14}N NMR shielding parameters in gaseous $^{14}\text{N}^{14}\text{NO}$ over the full pressure range 2.2 – 34.2 atm (0.09 – 1.41 mol/L). Simple analysis of these linear functions allows the virial coefficients σ_0 and σ_1 in gaseous nitrous oxide $^{14}\text{N}^{14}\text{NO}$ to be determined (see Table 3). There is a clear difference between the density coefficients σ_1 of NNO-NNO interactions for both nitrogen atoms.

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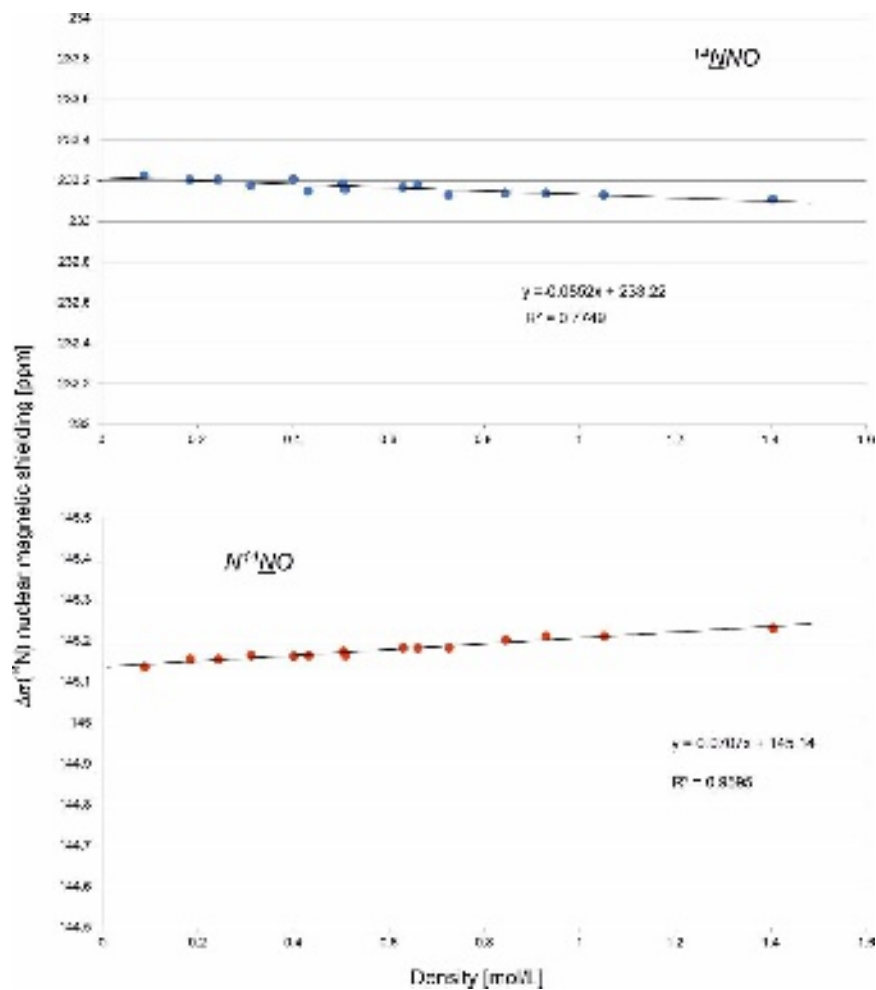


Figure 2. ^{14}N NMR shielding values plotted against the gaseous density of pure nitrous oxide ($^{14}\text{N}^{14}\text{NO}$).

For deuterated ammonia species we used chemical shifts shown in the spectra of Figure 3. Some previously reported results are also included. Neat liquid CH_3NO_2 (which was previously recommended and often applied) is used as a nitrogen NMR reference - $\sigma_0(^{14}/^{15}\text{N}) = -131.98$ ppm. On the basis of this data, the assignments of absolute shielding in the condensed phase can be introduced. It is worth mentioning that the chemical shifts of liquid substances should be corrected by the magnetic susceptibility effect using density and molar susceptibility factors. The results for water solutions of ammonium ions salts can be used as secondary references in the chemical shift scale of nitrogen spectra. They do not include susceptibility impact and are marked by asterisks (*). The experimental data considers both nitrogen isotopes: ^{14}N and ^{15}N , because of the small primary isotope effect compared to the quoted errors.

Table 3. $^{14/15}\text{N}$ nuclear magnetic shielding of gaseous and liquid substances (in ppm).

Substance	δ_0 (300K)	$\sigma_0(^{14}\text{N}/^{15}\text{N}, 300\text{K})$	Reference
NH_3		264.54(5)	[25]
	-398.67	266.784	[This work]
NH_2D		267.40(1)	
NHD_2		268.00(1)	
ND_3		268.61(1)	
N_2	-72.53	-59.36	[25]
	-70.83	-61.06	[38]
	-70.73(1)	-61.16(1)	[This work]
$\underline{\text{N}}\text{NO}$	-233.63	101.74	[25]
	-231.01(1)	99.12(1)	[This work]
$\text{N}\underline{\text{N}}\text{O}$	-145.17	13.28	[25]
	-142.93(1)	11.04(1)	[This work]
HCN	-113.73	-18.16	[25]
NF_3	-7.79(5)	-124.10(5)	[This work]
CH_3NH_2	-383.76(5)	251.78(5)	[39]
CH_3CN	-138.52(1)	-6.63(1)	[40]
$(^{13}\text{CH}_3)_2\text{NCHO}$	-287.53(9)	155.64(9)	[41]
$\text{CH}_3\text{NO}_2(\text{liquid})$	0.00	-131.89(1)	[This work]
$\text{NH}_3(\text{liquid})$	-382.10(10)	250.21(10)	
$\underline{\text{N}}\text{H}_4\text{NO}_3(\text{saturated})$	-360.65	228.76*	
$\text{NH}_4\underline{\text{N}}\text{O}_3(\text{saturated})$	-5.08	-126.81*	
$\text{NH}_4\text{Cl}(\text{saturated})$	-356.61	224.72*	

The original gas phase results, presented above, are well suited for comparison with relativistic calculations of nitrogen shielding constants. Up to now, this has been possible only for nitrogen trifluoride NF_3 : $\sigma(\text{N})=-125.95$ ppm⁴² where a 1.5% discrepancy with our experimental value has been found.

The gaseous sample with equimolecular amounts of $^{15}\text{NH}_3$ and $^{14}\text{ND}_3$ gases provided an opportunity to analyse isotope effects caused by the exchange of deuterium atoms. The secondary isotope effects on chemical shifts are: $^1\Delta^{15}\text{N}(^{15}\text{NH}_3, ^{15}\text{NH}_2\text{D})=-0.613(7)$ ppm, $^1\Delta^{15}\text{N}(^{15}\text{NH}_2\text{D}, ^{15}\text{NHD}_2)=-0.606(7)$ ppm and $^1\Delta^{15}\text{N}(^{15}\text{NHD}_2, ^{15}\text{ND}_3)=-0.601(7)$ ppm showing the small nonadditivity effect. ^{15}N nuclear magnetic shielding constants in ammonia molecules increase with the molecular mass of molecules, according to the usual behavior (see Table 3).

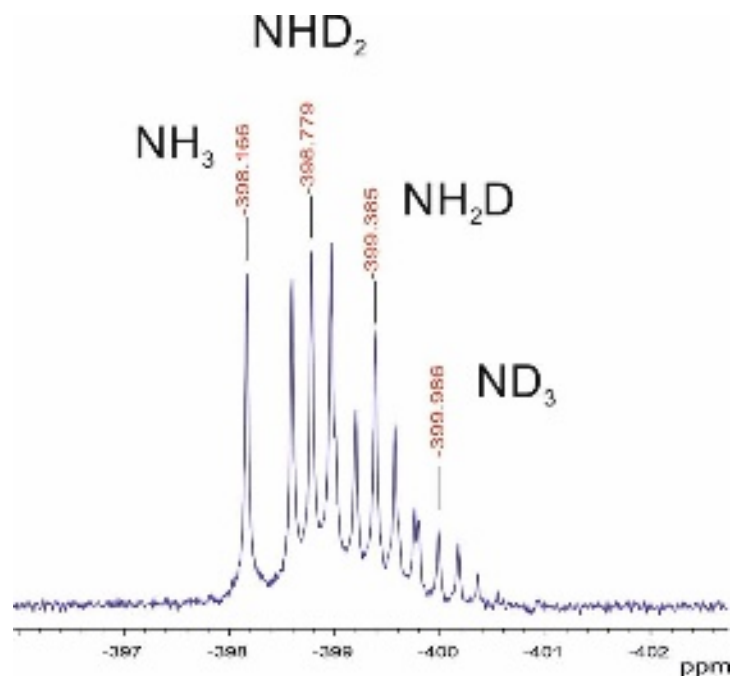


Figure 3. ^{15}N NMR spectrum of $^{15}\text{NH}_3/^{15}\text{NH}_2\text{D}/^{15}\text{NHD}_2/^{15}\text{ND}_3$ gaseous mixture sample at 7.05 atm recorded at 50.745 MHz. Signals recorded with digital resolution ~ 0.33 Hz, *i.e.* 0.007 ppm.

V. CONCLUSIONS

We carried out highly accurate theoretical-calculations of shielding constants in ammonia molecules included very accurate relativistic effects for the first time. This was performed on top of a new scheme that consider relativistic and electron correlation effects, together with zero-point vibrational corrections and temperature effects. The new calculated values of shielding constants of the isolated $^{14}\text{NH}_3$ molecule are $-\sigma_0(^1\text{H})=31.332$ ppm and $\sigma_0(^{14}\text{N})=266.780$ ppm, and $\sigma_0(^1\text{H})=31.333$ ppm and $\sigma_0(^{15}\text{N})=266.788$ ppm for the $^{15}\text{NH}_3$ molecule. The corresponding absolute shielding constants obtained from *ab initio* calculations

were discussed in detail. Interestingly the primary isotope effect on shielding and/or chemical shifts is very small and can be neglected in most cases.

The analysis of ^3He , ^1H and $^{14/15}\text{N}$ NMR spectra of ^3He - $^{14/15}\text{NH}_3$ gaseous mixtures was carried out in the context of nuclear magnetic moments. Accurate nuclear magnetic shielding constants were used for getting perfect values of ^{14}N and ^{15}N dipole moments:

$\mu(^{14}\text{N})=0.4035737(10)\mu_{\text{N}}$ and $\mu(^{15}\text{N})=-0.28305794(72)\mu_{\text{N}}$. The main source of errors of these values arises from the uncertainty of shielding values. The gas phase results were extrapolated to the zero-density limit and appropriate shielding values for isolated ammonia $^{14/15}\text{NH}_3$ molecules were defined from our theoretical results. The newest and best ever nitrogen absolute shielding scale is then introduced, where shielding of liquid CH_3NO_2 at 300K as an external reference is $\sigma(^{14/15}\text{N})=-131.98$ ppm. Our investigations displace the entire nitrogen scale in a higher shielding direction by ~ 2 ppm in contrast to earlier results. Absolute shielding values from the gas phase measurements were given in a new shielding scale for several nitrogen-containing substances: N_2 , NF_3 , HCN , N_2O , CH_3CN , CH_3NH_2 , $(\text{CH}_3)_2\text{NCHO}$. The deuterium substitution in $^{15}\text{NH}_3$ leads to valuable isotope effects measured on the ^{15}N nucleus ≈ -0.60 ppm with a small nonadditivity effect.

Our newest NMR spectroscopy experiments performed in gaseous mixtures with ^3He atoms, confirm the usefulness of the “helium” method in establishing absolute shielding values for nuclei in gaseous molecules.

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Conflict of Interest

The authors have no conflicts to disclose.

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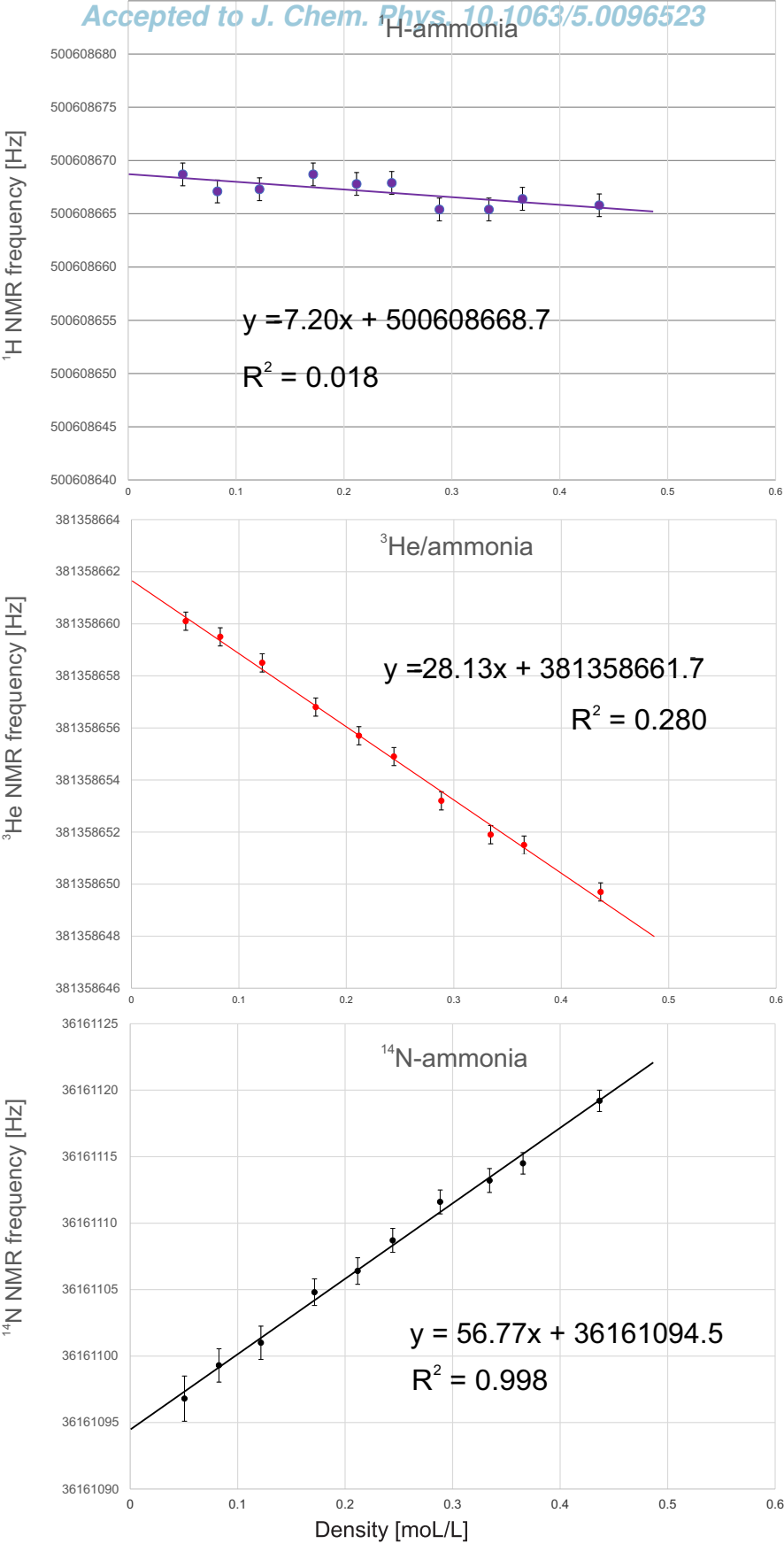
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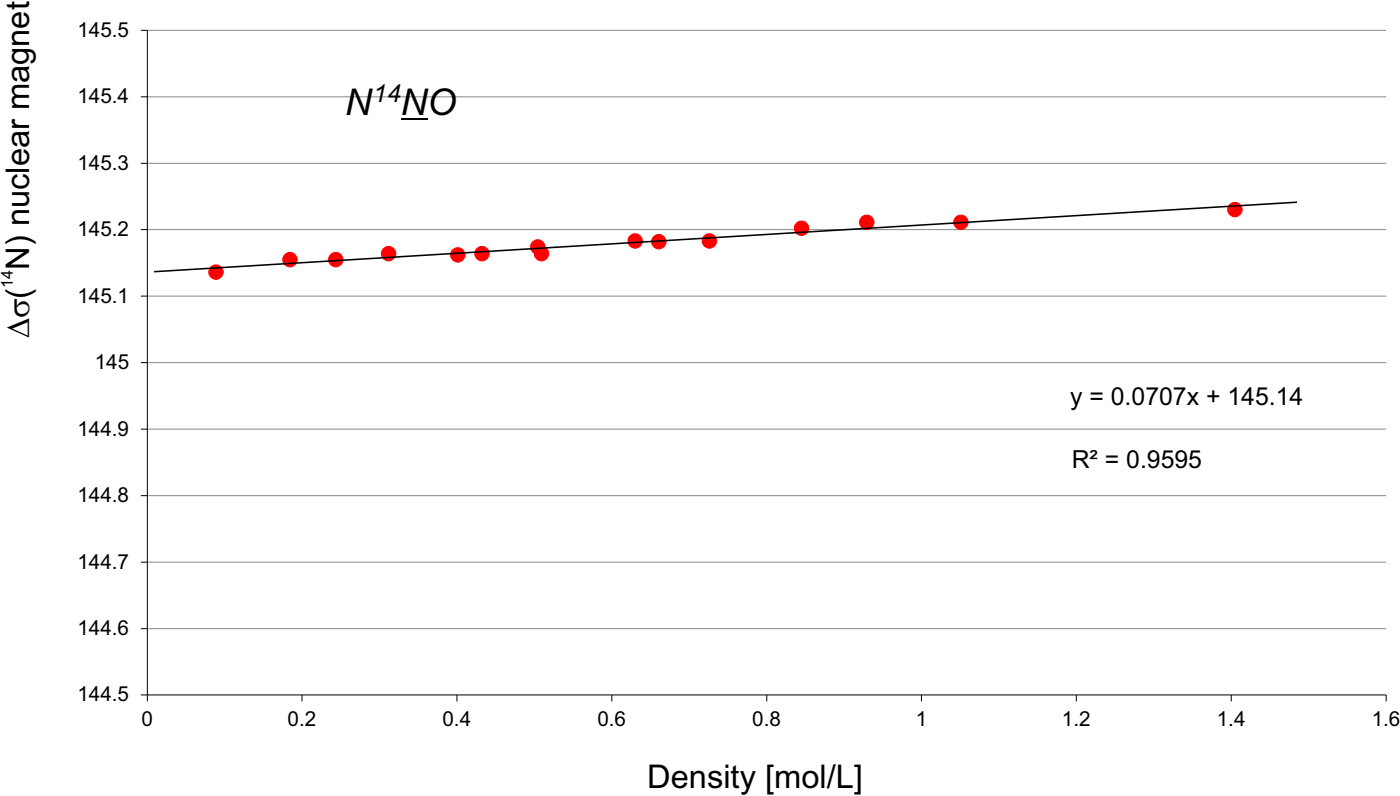
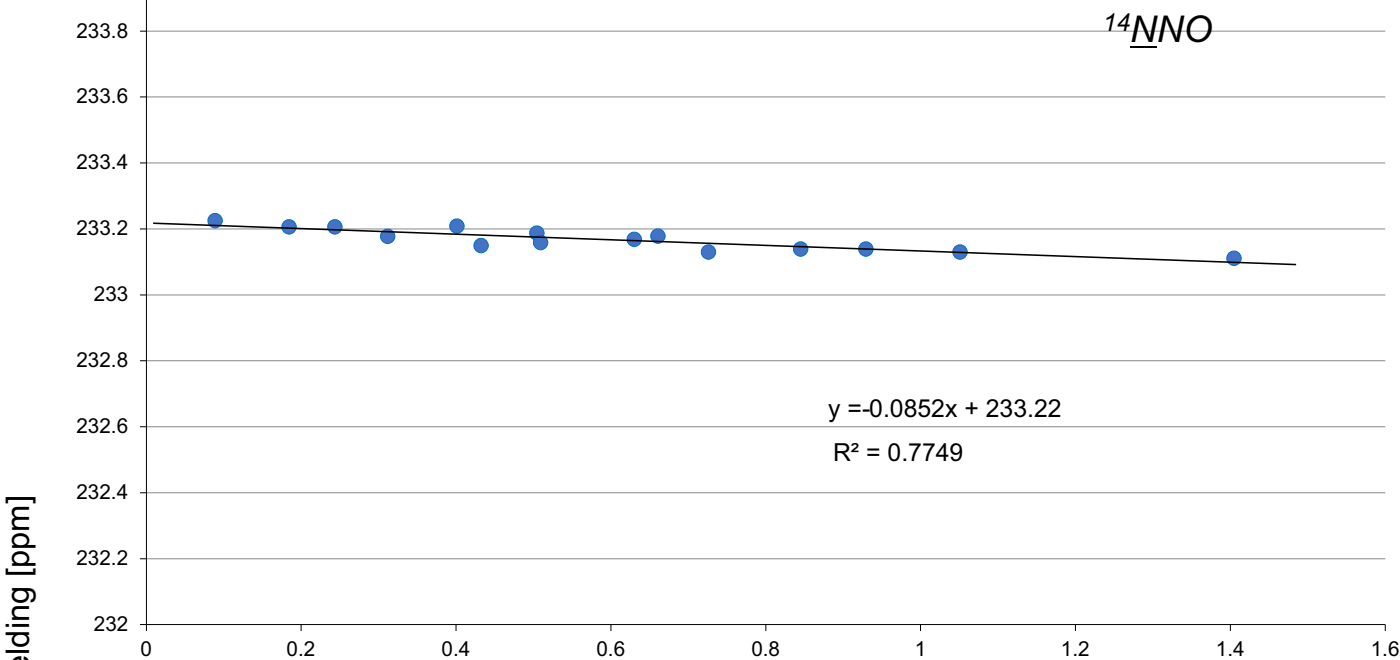
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