

## Dinitrogen as a possible internal standard for nitrogen nuclear magnetic resonance

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### Abstract

The potential applicability of dinitrogen as an internal nitrogen nuclear magnetic resonance standard is assessed by means of bulk susceptibility corrected measurements of its nitrogen shielding in 13 solvents. The observed range of nitrogen shieldings spans about 2 ppm. This range is comparable to the margin of error found for the external referencing technique when the latter is employed without bulk susceptibility corrections.

### Introduction

With few exceptions external standards are commonly used for referencing nitrogen nuclear magnetic resonance (NMR) spectra [1]. The main technique employed uses concentric cylindrical tubes, alternatively sample replacement may be used. The recommended external standard is neat nitromethane [1]. This situation results from the fact that to date solvent effects on nitrogen shieldings have been found to be large, usually in excess of 10 ppm, and this precludes the use of internal reference materials for nitrogen NMR. However, the price paid results from differences in the bulk susceptibility for the standard and substance under investigation. For superconducting systems with the sample tube parallel to the magnetic field axes, bulk susceptibility effects do not exceed 3 ppm; and about 1.5 ppm, and of opposite sign, for electromagnet systems where the magnetic field is applied in the direction perpendicular to that of the sample tube.

All of the above comments are valid only when paramagnetic materials or impurities are absent from the sample and reference under investigation.

For accurate studies it is necessary to correct for bulk susceptibility effects by calculating corrections under the assumption that the bulk susceptibility of the sample studied is the same as that of the solvent used.

If internal standards are employed then the problem of bulk susceptibilities is removed since the sample and the reference materials experience the same bulk susceptibility effects from the solution used. However, the solvent and possibly the solute, may effect the NMR shielding of the reference. Such influences are quite large in nitrogen NMR as mentioned previously [1]. An ideal case would be to include the use of a chemically inert standard whose nitrogen shielding is immune to solvent and other intermolecular effects. Recently this question has been revived [2] and dinitrogen ( $N_2$ ) has been proposed as a suitable internal standard for nitrogen NMR measurements.

Dinitrogen is present as an impurity in almost all samples with a sufficiently large concentration to be observed easily in  $^{14}N$  spectra as a sharp signal with a shielding of about +71 ppm from neat liquid nitromethane. For  $^{15}N$  NMR studies it would be necessary to expose the samples involved to a  $^{15}N$  labelled dinitrogen atmosphere in order to obtain a sufficiently strong reference peak. The recently published data [2] suggest that the shielding of dinitrogen in a variety of solvents is about 71.6 ppm with respect to nitromethane. However these results were obtained by use of an external reference standard without correction for bulk susceptibility effects. In the present work we report the results of precise dinitrogen NMR shielding measurements which include correction for bulk susceptibility effects and careful control of temperature. This permits us to draw some general conclusions on the possible applicability of the use of dinitrogen as a suitable internal standard for nitrogen NMR studies.

### Results and discussion

The results of our nitrogen shielding measurements for dinitrogen in thirteen solvents are presented in Table 1. The solvents chosen encompass a wide range of properties such as hydrogen bonding and polarity. As shown in Table 1 the solvent induced variations, in the nitrogen shielding of dinitrogen in solution are not very large but are significant and span a range of about 2 ppm for the chosen solvents. No obvious correlation exists between the observed nitrogen shielding and the solvent properties of the solvents used. For example, both water and  $CF_3CH_2OH$  are quite polar and are strong hydrogen bond donors whereas they act as solvents at the opposite ends of the shielding range for dinitrogen given in Table 1.



TABLE 1

Nitrogen NMR shieldings of dinitrogen in solutions corrected for bulk susceptibility effects

All data relate to saturated solutions at  $+35.0 \pm 0.2^\circ \text{C}$ 

Solvent used	$\text{N}_2$ shielding (ppm) referred to neat nitromethane <sup>a</sup>
$\text{CHCl}_3$	+69.6
Water	+69.6
DMSO	+69.8
$\text{CCl}_4$	+69.8
$\text{CH}_2\text{Cl}_2$	+69.9
Cyclohexane	+70.2
Dioxane	+70.2
Benzene	+70.4
Ethanol	+70.4
Acetone	+70.5
Diethylether	+70.6
Methanol	+70.8
$\text{CF}_3\text{CH}_2\text{OH}$	+71.5

<sup>a</sup> The positive values relate to an increase in shielding with respect to that of nitromethane. The accuracy of the results after including all corrections as described in the experimental section is better than 0.1 ppm.

A further point is that the nitrogen shieldings for dinitrogen in solutions in DMSO and acetone differ by more than 1 ppm, both of these solvents are strongly polar and are not hydrogen bond donors. Curiously enough the nitrogen shielding observed for the solution of dinitrogen in an inert hydrocarbon solvent (cyclohexane) is found close to the centre of the range of the solvent induced variations.

The range of solvent induced effects on the shielding of dinitrogen in the present work is about 2 ppm which is significant and comparable to the range of bulk susceptibility effects, about 3 ppm, if neat nitromethane is used as an external reference. Thus as an internal standard dinitrogen does not offer any significant experimental advantage over the external referencing technique used without bulk susceptibility corrections. Obviously the latter technique is particularly advantageous when the bulk susceptibility corrections are included. The previously reported [2] uncorrected, shieldings of dinitrogen giving a value of about 71.6 ppm in a variety of solvents appear to arise from a fortuitous cancellation of solvent and bulk susceptibility effects on the nitrogen shielding.

## Experimental

The samples studied were prepared by passing pure, dry,  $N_2$  through the solvents concerned to produce saturated solutions. Attention was paid to solvent purity, they were dried where applicable. The alcohols were distilled over magnesium and the chlorinated solvents were passed through a column of basic alumina directly before use. Benzene was distilled over  $P_2O_5$ , DMSO was distilled over calcium hydride and diethyl ether was distilled over sodium.

The nitrogen shielding measurements were made by high-precision  $^{14}N$  pulsed Fourier transform (PFT) NMR methods at a field which gives the nitrogen signal of neat nitromethane at a frequency of 36.141524 MHz. The magnetic field in question produces the resonance of a bare nitrogen nucleus at 36.136826 MHz [1]. All measurements were taken at  $35.0 \pm 0.2^\circ C$  which is maintained by a VT unit on a Bruker AM 500 instrument. Concentric tubes, 10/4 mm were employed, the inner one containing a 0.3 M solution of nitromethane in acetone- $d_6$  which provides both a deuterium lock, and our standard. This reference solution was purged of dinitrogen by the passage of dry argon gas for a period of several hours and gave rise to no observable dinitrogen signal. The nitrogen shielding of the 0.3 M solution of nitromethane has been measured by means of spherical concentric containers in order to remove bulk susceptibility effects on nitrogen shielding, and is found to be 0.77 ppm [3] with respect to that of neat nitromethane. The shielding data given in Table 1 are with respect to that of neat nitromethane after including bulk susceptibility corrections and 0.77 ppm for the standard used as described by

$$\sigma_N(\text{ref I}) = \sigma_N(\text{ref II}) + 0.77 - 1/3(\chi_{\text{ref II}} - \chi_{\text{sample}})$$

Where ref I is neat liquid nitromethane, ref II is a 0.3 M solution of nitromethane in acetone- $d_6$  and  $\chi$  is the volume magnetic susceptibility in SI units [1]. The measurements were taken with the sample and reference tubes aligned parallel to the applied magnetic field. The following parameters were commonly used in the  $^{14}N$  measurements;  $90^\circ$  pulse corresponding to 40  $\mu s$ ; spectral width about 8 KHz with quadrature detection; acquisition time about 0.15; zero relaxation delay; and about 2000 accumulated scans per spectrum. The  $^{14}N$  peak positions were obtained by means of a Lorentzian line-shape fitting procedure applied independently to the nitromethane signal and to that of dinitrogen.

## References

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