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Theoretical Gas to Liquid Shift of ^{15}N Isotropic Nuclear Magnetic Shielding in Nitromethane using *Ab Initio* Molecular Dynamics and GIAO / GIPAW Calculations.

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Chemical shift requires the knowledge of both the sample and a reference magnetic shielding. In few cases as nitrogen (^{15}N), the standard experimental reference corresponds to its liquid phase. Theoretical estimate of NMR magnetic shielding parameters of compounds in their liquid phase is then mandatory but usually replaced by an easily-get gas phase value, forbidding direct comparisons with experiments. We propose here to combine *ab initio* Molecular Dynamic simulations with the calculations of magnetic shielding using GIAO approach on extracted cluster's structures from MD. Using several computational strategies, we manage to accurately calculate ^{15}N magnetic shielding of nitromethane in its liquid phase. Theoretical comparison between liquid and gas phase allows us to extrapolate an experimental value for the ^{15}N magnetic shielding of nitromethane in gas phase between -121.8 and -120.8 ppm.

Introduction.

NMR isotropic chemical shifts are defined according to an external reference using the following standard expression:

$$\delta_{iso}(sample) = \sigma_{iso}(ref) - \sigma_{iso}(sample).$$

$\delta_{iso}(sample)$ is the isotropic chemical shift of the sample, $\sigma_{iso}(ref)$ and $\sigma_{iso}(sample)$ are the isotropic magnetic shieldings of the external reference and the sample, respectively. For instance, tetramethylsilane (TMS) is the standard reference used for ^{13}C or ^1H , when for ^{15}N nuclei, liquid ammonia ($\text{NH}_3(\text{liq})$) or liquid nitromethane ($\text{CH}_3\text{NO}_2(\text{liq})$) are used.

Ideally, isotropic chemical shift calculations need to determine both isotropic magnetic shieldings at the same level of theory. This means that when changing the electronic calculation method and/or the basis set used to describe the electronic density, one has to recalculate the magnetic shielding of the reference, for complete consistency. It is currently admitted that even if magnetic shieldings may not be accurately computed for complex systems using standard Density Functional Theory (DFT) methods, accurate chemical shifts are still obtained due to errors cancelation. Thus, using the same theoretical approach for both systems remains the safest method to compute chemical shifts with good accuracy. In these conditions, reference compounds and the chemical shift calculations does not rely on any experimental parameter. This procedure is most of the time respected for ^{13}C or ^1H NMR spectroscopy. However, standard value of the isotropic magnetic shielding extracted from temperature dependent measurements is generally employed for ^{15}N nucleus. Indeed, proper calculation of the ^{15}N reference still remains a theoretical challenge since both ammonia and nitromethane references are taken in their liquid state while

standard quantum chemical calculations are mainly performed in the gas phase at 0 K. When theoretical magnetic shielding of reference is used to calculate ^{15}N chemical shift, it is not surprising to observe errors up to 20 or 30 ppm compared to experiments¹. This inaccuracy is consistent to the gas to liquid shift that is experimentally observed for ammonia and nitromethane^{2, 3}. For the latter, no gas phase magnetic shielding has been measured. However, ^{15}N magnetic shielding of nitromethane obtained in dilute solution in cyclohexane exhibits a difference of about 9.0 ppm compared to liquid state⁴ and is often considered as the gas phase value.

Another approach that allows to determine the magnetic shielding of the reference is to use a set of several molecules for which experimental chemical shift are known. The linear correlation between theoretical magnetic shieldings and experimental chemical shifts of all these substances gives the theoretical magnetic shielding of the reference compound by taking the intercept, considering that the slope is not far from 1. However, this means that this correlation has to be performed each time the computational setting is modified⁵⁻⁷.

Because of this, it is necessary to model the liquid phase and to perform magnetic shielding calculations on top of these models. In this article, several different strategies are proposed to determine accurate values of ^{15}N magnetic shielding of nitromethane in its liquid phase. A first approach is based on cluster type calculations on a finite number of molecules to mimic the liquid conditions. A second strategy is based on calculations using solvent continuum model in order to reproduce the liquid medium. The third strategy consists in modelling the liquid state by using *ab initio* molecular dynamic (AIMD) simulations within periodic boundary condition. This approach intends for molecular structures' generation that are used

afterwards for cluster type NMR calculations as it was already proposed in the case of ^1H NMR of liquid water^{8,9}.

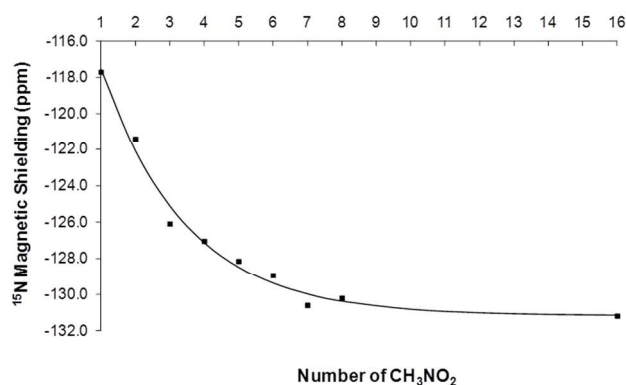


Fig. 1 Variation of ^{15}N magnetic shielding of CH_3NO_2 calculated using B3LYP/6-31g(d,p)//B3LYP/6-31G(d,p) method as a function of molecule number.

Computational details.

All molecular and cluster type calculations (geometry optimization and NMR properties determination) have been carried out using the Gaussian09 suite of programs¹⁰.

In the first part of this study, two Density Functional Theory (DFT) approaches have been considered for geometry optimization of nitromethane (CH_3NO_2)_{n,n=1-8} clusters and NMR magnetic shielding tensors calculations. The Generalized Gradient Approximation PBE^{11, 12} and hybrid B3LYP^{13, 14} Density Functional Theory (DFT) approaches were used with either Pople type double ζ basis set augmented by polarization functions on all atoms (namely 6-31G(d,p)) or Pople type triple ζ basis set augmented by polarization and diffuse functions on all atoms (namely 6-311++G(d,p))¹⁵. NMR magnetic shielding tensors have been computed using the Gauge Including Atomic Orbital method (GIAO) for the numerous advantages it offers¹⁶⁻²¹. Using the same basis sets, 4 sets of calculations were performed by combining DFT approaches for geometry optimization and for NMR calculations. We used the following standard notation in order to describe the theoretical framework: NMR Calculation Method//Geometry Optimization Method. These four computational schemes allow us to analyze the influence of several parameters on the calculation of NMR ^{15}N magnetic shielding.

Secondly, we manage to model nitromethane in several solvents - cyclohexane, acetone and nitromethane - for which experimental data are available⁴, by using continuum solvation model namely SMD²². In the last case, nitromethane in nitromethane solvent, calculations can be considered as a different way to model the liquid phase. For all three solute-solvent systems, geometry optimization and NMR calculations have been performed using the same theoretical approaches than the ones used previously. Default values as implemented in Gaussian 09 have been used for dielectric constants of the three solvents ($\epsilon_{\text{cyclohexane}} = 2.0165$, $\epsilon_{\text{acetone}} = 20.493$, $\epsilon_{\text{nitromethane}} = 36.562$).

Because vibrational corrections can be important for the accurate computation of magnetic shielding²³⁻²⁵, we decided to include such corrections by mean of *ab initio* molecular dynamics in the

gas phase or within solvation model SMD. For this purpose, our own molecular code²⁶ that is coupled to Gaussian 09¹⁰ for gradient calculations has been employed. Born-Oppenheimer molecular dynamic were carried out for 10 ps with the Velocity-Verlet integration scheme using a time step of 0.5 fs. Dynamic simulations have been performed at a 298K temperature that was controlled by mean of a Nosé-Hoover chain of thermostats^{27, 28}. Because not all liquid phase can be modelled using SMD solvent approach (ex. liquid water or liquid ammonia), molecular dynamics within periodic boundary condition has also been considered in order to model nitromethane liquid state. We have carried out DFT simulations of the liquid phase using the Vienna *ab initio* simulation package (VASP)^{29, 30}. The code uses the full-potential Projector Augmented Waves (PAW) framework^{31, 32}. Exchange-correlation effects have been approximated by using the non-spin polarized version of PBE^{11, 12}. Born-Oppenheimer molecular dynamics were carried out, under constant volume and temperature using Nosé thermostat³³. Liquid nitromethane simulations were performed first on a model containing 8 molecules in a cubic box of 9.0 Å of length for a density value of 1.1 g.cm⁻³ at 298 K. A dynamical time step of 0.5 fs was employed for all runs, to obtain trajectories of 10 ps, thanks to a first-order Verlet extrapolation scheme³⁴. Initial geometries and velocities were randomly chosen. A kinetic energy cut-off of 400 eV was found to be sufficient to achieve a total energy convergence within several meV considering *k*-point sampling, for which a Γ -centered grid of (3x3x3) points was used. Considering the smearing issue, during the molecular dynamics runs, a Gaussian smearing was applied with a width of 0.1 eV. In order to evaluate the validity of our first liquid phase simulation, a second model containing 20 molecules in a box of 12.12 Å of length has been employed with a Γ -centered grid of (2x2x2) for *k*-point sampling. MD was also performed on single molecule using supercell approach with a box size of 15 Å to mimic gas phase.

Finally, calculations have been performed on 5000 snapshots extracted from all molecular dynamics trajectories using GIAO cluster approach. For each trajectory, the first 5 ps have been rejected and each snapshot has been extracted every femtoseconds during the last 5 picoseconds. In the case of molecular dynamics performed on liquid model using VASP, the final ^{15}N isotropic value has been calculated by averaging the shielding of the central molecule, the one that remains in the centre of the box for each snapshot of the MD. Indeed this molecule is the one that feels most strongly the environment effect in the cluster extraction procedure.

Finally, NMR calculations using the GIPAW³⁵⁻³⁷ method were performed first on the molecule in gas phase but also on the very last geometry provided by the MD run. In these calculations all atoms were fully relaxed to yield forces on individual atoms smaller than 0.02 eV/Å. In order to obtain converged shielding values, a higher cut-off energy was chosen 600 eV, in conjunction with a convergence threshold of 10⁻¹⁰ on the energy value. Ideally, a statistical approach would also have to be performed using the GIPAW calculations. However the corresponding computational cost does not allow for such a study. Indeed GIPAW calculations are extremely time consuming compare to GIAO, with approximately a factor of 30 (for CPU

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Table 1 ¹⁵N magnetic shieldings calculated on single molecules or extrapolated from cluster type calculations. Values in parenthesis are the chemical shift calculated using liquid nitromethane as a reference (first value SMD model and second value "cluster type" calculation). Except for GIPAW for which calculations have been performed using Periodic Boundary Conditions using VASP program, all calculations have been performed using GIAO approach.

| NMR// Opt | Exp. ⁴ | GIPAW | | 6-31G(d,p) | | | 6-311++G(d,p) | | | |
|-----------------------------|-------------------------|-------------------|-----------------------------|----------------------------|-----------------------------|----------------------------|-----------------------------|-------------------------|-----------------------------|-----------------------------|
| | | PBE// PBE | B3LYP// B3LYP | PBE// B3LYP | B3LYP// PBE | PBE// PBE | B3LYP// B3LYP | PBE// B3LYP | B3LYP// PBE | PBE// PBE |
| Gas | - | -147.8 (+12.6) | -117.7 (+13.3 /+13.5) | -86.7 (+12.0 /+12.5) | -126.5 (+13.9 /+12.9) | -93.3 (+12.5 /+12.0) | -152.6 (+17.0 /+12.1) | -117.6 (+15.6) | -162.0 (+17.9 /+11.8) | -124.9 (+16.2 /+10.7) |
| Cyclohexane (SMD) | -126.8 (+9.05) | - | -122.8 (+8.2) | -91.3 (+7.4) | -131.8 (+8.6) | -98.1 (+7.7) | -158.9 (+10.7) | -123.6 (+9.6) | -168.9 (+11.0) | -131.2 (+9.9) |
| Acetone (SMD) | -135.03 (+0.77) | - | -130.5 (+0.5) | -98.2 (+0.5) | -139.9 (+0.5) | -105.3 (+0.5) | -168.9 (+0.7) | -132.5 (+0.7) | -179.2 (+0.7) | -140.5 (+0.6) |
| Liquid (SMD) | -135.8 (0.0) | - | -131.0 (0.0) | -98.7 (0.0) | -140.4 (0.0) | -105.8 (0.0) | -169.6 (0.0) | -133.2 (0.0) | -179.9 (0.0) | -141.1 (0.0) |
| Liquid "Cluster type" | -135.8 (0.0) | -160.4 (0.0) | -131.2 (-0.2) | -99.2 (+0.5) | -139.4 (+1.0) | -105.3 (+0.5) | -164.7 (+4.9) | | -173.8 (+6.1) | -135.6 (+5.5) |

5 Time) between the two types of calculation performed on the same computational set (considering the 8 molecules box for GIPAW calculations). Nevertheless, calculation performed with periodic boundary conditions allows obtaining, in one step, a mean value over 8 molecules.

10 Results and discussion.

Static calculations.

The liquid phase modelling using nitromethane within SMD solvent model has been considered as our liquid reference for all molecular calculations. In the case of cluster type approach, geometry optimization and NMR calculation have been performed for each cluster (CH₃NO₂)_{n,n=1-8}. Because the magnetic shielding evolution exhibits a decreasing exponential behaviour as a function of molecules number (Figure 1), data have been fitted according to this function. The liquid phase magnetic shielding has been obtained by taking the asymptotic value.

For liquid phase modelling, both approaches (implicit nitromethane solvent or cluster type approach) almost lead to the same magnetic shielding value when using 6-31G(d,p) basis set if one computational scheme (Specific DFT method for geometry optimization and for NMR calculation) is considered (see Table 1). When the computational scheme is changed, the absolute magnetic shielding can be largely modified (up to 50 ppm), but the difference between SMD and cluster type approach remains consistent. When using triple zeta basis set, a decrease of almost 40 ppm is observed for all computational schemes compared to double zeta basis set calculations. Accordingly, while B3LYP/6-31G(d,p) NMR calculations are in good agreement compare to

experiment and PBE/6-31G(d,p) NMR computation are far from experimental data, the invert is observed when using triple zeta basis set (good agreement for PBE/6-311++G(d,p)). The difficulty to calculate nitromethane magnetic shielding as a function of basis sets is consistent with previous calculations reported in the literature³⁸ and might be correlated to the difficulty to correctly compute the electronic density on the -NO₂ chemical group. Due to a significant increase in the computation time when using triple zeta basis set, it is not suitable to use such basis set especially since we want to perform a lots of NMR calculations coupled with molecular dynamics (see next section). Moreover, a difference between 4 and 6 ppm is observed between the two ways to simulate the solvent in poorer agreement compared to calculations performed using a double zeta basis set.

Table 2 ¹⁵N magnetic shieldings calculated using GIAO approach. Values in parenthesis are the chemical shift calculated using liquid nitromethane as a reference.

| | Nitromethane (SMD) geometry | After full geometry optimization |
|-----------------------------|--------------------------------|-------------------------------------|
| Gas phase | -128.8 (+11.6) | -126.5 (+13.9) |
| Cyclohexane (SMD model) | -133.4 (+7.0) | -131.8 (+8.6) |
| Acetone (SMD model) | -139.8 (+0.6) | -139.9 (+0.5) |
| Nitromethane (SMD model) | -140.4 (0.0) | -140.4 (0.0) |

When comparing experimental and theoretical chemical shifts of nitromethane in acetone or cyclohexane solvent, a good accuracy is observed for calculations performed with both basis sets when

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Table 3 NO Bond lengths in Å. Values in parenthesis are the difference compare to liquid geometry. 'PBC/PBE' is related to calculations using Periodic Boundary Conditions using VASP.

| | B3LYP/ 6-31G(d,p) | PBE/6-31G(d,p) | PBE/6-31G(d,p) | PBC/PBE | PBC/PBE |
|-------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| | Static | Static | Dynamic | Static | Dynamic |
| Gas | 1.2267 (-0.0032) | 1.2367 (-0.0035) | 1.2390 (-0.0040) | 1.2387 (-0.0034) | 1.2404 (-0.0023) |
| Cyclohexane (SMD) | 1.2280 (-0.0019) | 1.2381 (-0.0021) | 1.2406 (-0.0024) | - | - |
| Acetone (SMD) | 1.2298 (-0.0001) | 1.2403 (+0.0001) | 1.2421 (-0.0009) | - | - |
| Liquid (SMD or Cluster) | 1.2299 | 1.2402 | 1.2430 | 1.2421 | 1.2427 |

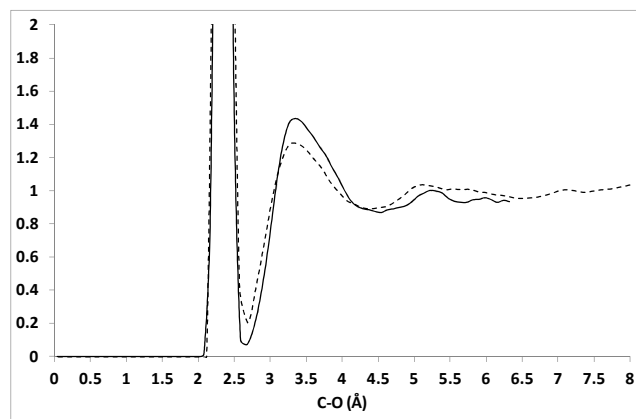
^a Footnote text.

5 using nitromethane implicit SMD solvent as reference for chemical shifts calculations. For the nitromethane-acetone system, theoretical calculations are in very good agreement compare to experiment, while for cyclohexane solvent, a difference up to 2 ppm is observed (compare to the 9.05 ppm
10 experimental chemical shift). Considering that chemical shifts calculations using SMD solvent model exhibit a good accuracy compared to experiments, the chemical shift values computed for the gas phase significantly diverge from the cyclohexane solution value. This is in contradiction with the fact that dilute solution of
15 nitromethane in cyclohexane can be considered as the gas phase value⁴. The chemical shift value for the gas phase relative to the liquid state ranges between 12 and 14 ppm and from 16 and 17 ppm using 6-31G(d,p) and 6-311++G(d,p) basis set, respectively. In order to analyze the influence of geometry changes due to
20 environmental effect on magnetic shielding, NMR parameters calculations have been performed on the liquid phase SMD geometries. For acetone solvent, the magnetic shielding change is exclusively due to solvent effect on the electronic density (chemical shift without geometry optimization +0.6 ppm compare
25 to +0.5 after geometry optimization, see Table 2). Indeed when looking at the NO distance, no change is observed between nitromethane liquid phase and acetone solution (see Table 3). For cyclohexane solution, SMD calculation on liquid phase nitromethane geometry already induces an important increase of
30 the NMR magnetic shielding (+7.0 ppm). Geometry optimization using cyclohexane SMD model induces an additional increase of the magnetic shielding of 1.6 ppm. A similar behavior is also observed in the gas phase case. Gas phase calculation on the liquid phase geometry exhibits a chemical shift equal to +11.6
35 ppm compare to +13.9 ppm after gas phase geometry optimization (additional increase of +2.3 ppm). These can be interpreted according to the decrease of the NO bond length that is observed when dielectric constant of the solvent decreases (cf Table 3). Indeed, when NO bond length increases, a decrease of
40 the magnetic shielding is observed (increasing in absolute value). This allows us to interpret the behaviour as a function of DFT

functional when going from B3LYP to PBE. In this case, a large decrease of the magnetic shielding is observed in conjunction with a large increase of the NO bond length (see static values in
45 Table 1 & 3).

Ab initio molecular dynamics.

As can be seen in the previous section, ¹⁵N magnetic shielding can be subject of large variations as a function of geometric parameters, especially NO bond length. According to this, *ab*
50 *initio* molecular dynamics have been performed in order to better describe the specificity of liquid state taken at a finite temperature. First, molecular dynamics at the PBE/6-31G(d,p) level have been performed with or without simulating solvent effects using SMD approach. Compare to static calculations, an
55 increase of the NO bond lengths is observed with amplitudes around 0.002 Å (See Table 3). An increase of the CN bond length is also observed but depends on the nature of the solvent. It ranges from 0.006 to 0.01 Å (data not shown).



60 **Fig.2** Radial distribution function for CO pair of nitromethane. Molecular Dynamics within Periodic Boundary Conditions using 8 molecules (Solid line) and 20 molecules (dash line)

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Table 4 ^{15}N magnetic shieldings calculated using GIAO or GIPAW approaches. Static calculations have been obtained after geometry optimization. Dynamic value have been calculated by taking GIAO NMR Shielding averaged over AIMD snapshots (see text for details). Values in parenthesis are the chemical shift calculated using liquid nitromethane as a reference. 'Dynamic GTO' means *ab initio* molecular dynamic using Gaussian Type Orbitals performed with our own MD code. 'Dynamic PW' means *ab initio* molecular dynamic using plane wave basis set using VASP code.

| | Exp ^a | Static (GIAO) | Dynamic GTO (GIAO) | Dynamic PW (GIAO) | Static PW (GIPAW) |
|-------------------------|--------------------|-------------------|--------------------------|-------------------------|-------------------|
| Gas | - | -126.5 (+13.9) | -129.6 ± 14.6 (+15.0) | -132.6 ± 15.8 (+7.0) | -147.8 (+12.6) |
| Cyclohexane (SMD) | -126.8 (+9.05) | -131.8 (+8.6) | -135.2 ± 11.9 (+9.4) | | |
| Acetone (SMD) | -135.03 (+0.77) | -139.9 (+0.5) | -143.0 ± 11.9 (+1.6) | | |
| Liquid (SMD or Cluster) | -135.8 (0.0) | -140.4 (0.0) | -144.6 ± 10.4 (0.0) | -139.6 ± 15.8 (0.0) | -160.4 (0.0) |

^a Footnote text.

In the case of cluster approach, our previous calculations can be subject to caution due to the arbitrariness of the cluster geometries employed. If one wants to mimic the liquid phase, a single cluster configuration is definitely not sufficient. It is thus mandatory to sample "randomly" as many configurations as possible in order to describe the liquid phase accurately. This is generally performed using statistical analysis (molecular dynamics simulations or Monte Carlo sampling). Simulating liquid nitromethane remains a delicate task that needs specific cares in order to correctly reproduce specific structural characteristics. This is usually verified by examining the radial distribution function $g(r)$ of characteristic interatomic distances, in comparison with experimental data. When considering nitromethane liquid simulations under periodic boundary conditions, a good agreement is obtained with previous MD and experiments³⁹⁻⁴² even if our density is slightly smaller than the experimental one (1.11 and 1.14 g.cm⁻³, respectively). Indeed all principal features that characterize $g(r)$ functions are well reproduced by simulations (Figure 2 and S2). When molecular dynamics are performed with either 8 or 20 molecules in the box, no major differences can be observed for the radial distribution functions (Figure 2 and S2). Because the purpose of this work is not to completely characterize the liquid phase of nitromethane, we will not go further on the analysis of radial distribution functions.

NMR magnetic shielding calculations on MD snapshots.

As previously explained, 5000 structures have been extracted from MD simulations and average ^{15}N NMR values have been determined from NMR calculations on each snapshot. For each calculations, we used GIAO B3LYP/6-31G(d,p) approach because it presents the best ratio between shielding quality and calculation time. Results are reported in Table 4.

First, using SMD model in order to simulate solvent or liquid phase, a decrease of all magnetic shieldings is observed when compared to experiments. It is related to the increase of NO bond length when taking into account vibrational averaging. As for

static calculations, a very good agreement is obtained for nitromethane in cyclohexane solvent. However, a slight discrepancy is obtained for acetone solvent with a chemical shift two times larger than experiments that can be correlated to the variation of NO bond length observed (See table 3). Finally, MD simulations confirm our conclusion on gas phase magnetic shielding that is largely different from nitromethane in cyclohexane. Consequently, a new value is proposed for the experimental value of gas phase nitromethane that ranges between -121.8 and -120.8 ppm, 5 to 6 ppm above the value taken from cyclohexane solution.

For sake of comparison, GIPAW calculations have been undertaken on the very last structures obtained by MD calculations. Starting from these structures, geometry optimizations have been performed using a constant cell unit in order to maintain the density. In this series of calculations, while the sampling effect on the magnetic shielding value is missing, the liquid description using periodic boundary condition during geometry optimization and magnetic shielding calculation is kept. In order to determine gas to liquid shifts, magnetic shieldings have been also computed on isolated molecule within the supercell approach. Despite the fact that absolute magnetic shielding are larger than the one obtained using molecular approach, the gas to liquid shift that is computed is consistent with the ones obtained with previous computational strategies. The magnetic shielding is slightly smaller (+12.6 ppm) compare to others theoretical results but exhibits a larger value than the one proposed in the literature as the magnetic shielding obtained in dilute solution in cyclohexane (+ 9 ppm).

Conclusion.

We present several strategies in order to accurately calculate magnetic shielding of compounds in their liquid phase. Using a cluster type approach with a reduced number of molecules or using SMD solvent model in order to simulate liquid phase or by mean of periodic boundary conditions, we manage to calculate

similar value for gas-to-liquid shift of ^{15}N magnetic shieldings of nitromethane. These computational strategies might be employed with more or less success for the computation of NMR magnetic shielding of liquid phase compound depending on the nature of the intermolecular interactions. Indeed, when hydrogen bonds are present in the liquid state (H_2O for example), SMD approach might not be adequate. In order to specifically reproduce such intermolecular interaction, "cluster type" approach or Periodic Boundary Conditions calculations should be employed. Thus, accurate magnetic shielding should be obtained.

Moreover, based on our calculations, we propose a new experimental value for the ^{15}N magnetic shielding of nitromethane in its gas phase between -121,8 and -120,8 ppm. This value constitutes a correction of 5-6 ppm compare to the one usually employed experimentally.

Notes and references

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† Electronic Supplementary Information (ESI) available: Magnetic shielding variation as a function of cluster size using 6-311++G(d,p) basis set (S1). Selected radial distribution functions (S2). ^{15}N shielding average evolution as a function of the number of structures (S3). See DOI: 10.1039/b000000x/

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