Calculations of the ^{1}H NMR shifts for water and methanol clusters

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Magnetic shielding constants of hydroxyl protons in water and methanol hydrogen bonded clusters obtained at the SCF/GIAO level are presented. Our final results were computed with the 6-311++G(d,p) basis set. The effect of basis set on accuracy of calculated spectrum is discussed. All clusters exhibit small changes in the shielding of free hydroxyl protons compared to monomer. With increasing cluster size the downfield migration of the hydrogen bonded hydroxyl proton signal is observed. The results are discussed in terms of the ^{1}H NMR spectrum of hydrogen bonded liquids. Linear correlation between the chemical shift and inverse of the length of a hydrogen bond is also found.

1. INTRODUCTION

Alcohols are frequently used as examples in explanation of the shape of the ^{1}H NMR spectra. There are a few reasons. First of all there are large differences in the shielding of protons belonging to different groups – this leads to well separated signals in the NMR spectrum. Second, nuclei of the most abundant ^{12}C and ^{16}O isotopes are non–magnetic – spin–spin coupling only between protons has to be taken into account. Third, hydroxyl protons of different molecules are exchanged in the liquid phase – the influence of chemical exchange processes on the NMR spectrum can be demonstrated.

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Theoretical determination of the NMR spectra of molecules (see ref. [1] for recent review) can be performed even for large systems with modern *ab initio* quantum mechanical programs. It was shown [2] that in the case of ethanol, the SCF/GIAO/6-31G(d) approach applied to an isolated molecule reproduces reasonably well the experimental separations among three ^{1}H NMR signals in the gas phase. More accurate SCF/GIAO/6-311G(d,p) calculations [3] are capable of predicting chemical shifts of protons (δ_H relative to TMS). However, simulations of a spectrum for hydrogen bonded liquids, in particular the simulation of the location of the hydroxyl proton signal, is a more difficult task because of the presence of isolated molecules as well as their hydrogen bonded clusters M_n, n=1,2,... in the bulk phase. The relevant approach should be based on calculations of isotropic magnetic shieldings constants σ_H of their hydroxyl protons – the difference between σ_H^{TMS} and the population weighted average of σ_H is the relevant measure of the chemical shift δ_H in a liquid phase.

Ethanol was already subject of such calculations. The populations [4] were estimated within the so-called Quantum Cluster Equilibrium (QCE) model of liquids [5]. The authors used the SCF approach with a few small basis sets to evaluate the clusters' properties. The isotropic shielding constants were calculated [2] at the SCF/GIAO/6-31G(d) level of theory. The upfield migration of the hydroxyl proton signal with increasing temperature was correctly predicted, although the absolute values of the chemical shifts were significantly underestimated. The problem of accuracy of these calculations was already discussed in detail [3]. In particular, the presence of diffuse functions in the basis set was shown to be of crucial importance in the accurate determination of magnetic shielding constant of the hydroxyl proton in ethanol clusters. The ^{1}H NMR chemical shifts of water clusters were also studied (see e.g. [6] and references therein). However, no consistent, high–level data for the subsequent use in the QCE treatment of liquid water are available at present.

In this paper we report isotropic proton magnetic shielding constants in water and methanol clusters: $(H_2O)_n$, n=1,2,3,4,5,6,7,8,12 and $(CH_3OH)_n$, n=1,2,3,4,5,6,7. The SCF/GIAO approach was used along with extended basis sets. The effect of incorporating diffuse functions in the basis set is analysed. Comparison with DFT/GIAO calculations on methanol is also carried out. We expect, that the reported values are much more accurate than the data available up to date. When used with appropriate cluster populations the theoretical spectrum of liquid water and methanol will be obtained. Theoretical description of the ^{1}H NMR spectra of the hydrogen bonded liquids is one of the primary goals of the research in our group. In Section 2 the details of *ab initio*

calculations are given. In Section 3 the isotropic magnetic shielding constants obtained at the SCF/GIAO level of theory are reported and discussed. They are compared to the DFT/GIAO calculations in Section 4. In Section 5 we state our conclusions.

2. COMPUTATIONAL PROCEDURE

The chemical shifts of nuclei are very sensitive to changes in molecular geometry. It was shown that in the case of ethanol molecule [3] the change in the OH bond length as small as 1% causes the change in the chemical shift δ_H of a hydroxyl proton close to 0.4 ppm. Optimized geometries were proved to be preferable for the calculation of the chemical shifts. Accurate geometries of water and methanol clusters, obtained at the Density Functional Theory (DFT) [7] level with the B3LYP exchange–correlation potential [8,9] and the 6-311G(d,p) basis set [10], were reported in the accompanying paper [11]. We use them here in calculations of NMR chemical shifts.

The gauge including atomic orbitals (GIAO) method [12-14] was used for all NMR calculations. The isotropic magnetic shielding constants were obtained at the SCF/GIAO level with the 6-311G(d,p) [15] and 6-311++G(d,p) [10] basis sets for water and methanol. It was shown recently [6], that the magnetic shielding constants of protons in water molecule computed at the SCF/GIAO level are as good as these computed at correlated level (see eg. [1,16,17]). SCF/GIAO is also capable of predicting the changes in the proton shielding due to the hydrogen bond formation in water dimer. However, correlated methods are needed in the calculation of the NMR magnetic shielding constants of heavy atoms. The 6-311G(d,p) basis set was shown to give magnetic shielding constants of protons in water molecule close to the basis set limit. For the water dimer diffuse functions are also important. It is worth – while to note, that the counterpoise correction does not change the magnetic shielding constant of a hydrogen bonded pronon in water dimer [6].

All calculations reported in this paper were performed with the parallel version of the *ab initio* quantum chemistry PQS package [18,19] implemented for a cluster of Pentium II/400 MHz PC machines. The maximum speed-up obtained with 12 CPUs was about 11 as compared to the single processor run.

3. THE SCF/GIAO CALCULATIONS

In this paper we present the calculated ^1H magnetic shielding constants and chemical shifts relative to TMS for the series of water and methanol clusters at the SCF/GIAO/6-311G(d,p) and SCF/GIAO/6-311++G(d,p) levels of theory. The results are summarized in Tables 1 and 2.

Tab. 1. The average SCF/GIAO ¹H isotropic magnetic shielding constants[a] and chemical shifts δ (relative to TMS) in water clusters (in ppm) calculated at DFT/B3LYP/6-311G(d,p) optimized geometries

Structure	SCF/GIAO/6-311G(d,p)[b]				SCF/GIAO/6-311++G(d,p)[c]			
	$\sigma_H^{(f)}$	$\sigma_H^{(h)}$	σ_H	δ	$\sigma_H^{(f)}$	$\sigma_H^{(h)}$	σ_H	δ
Monomer	31.33		31.33	0.92	31.13		31.13	1.09
Dimer	31.12	28.25	30.40	1.85	30.87	27.82	30.11	2.11
Trimer-1	31.44	26.92	29.18	3.07	31.20	26.42	28.81	3.41
Trimer-2	31.22	26.87	29.05	3.20	30.97	26.38	28.67	3.55
Tetramer	31.26	25.00	28.13	4.12	30.90	24.42	27.66	4.56
Pentamer	31.38	24.31	27.85	4.40	31.00	23.76	27.38	4.84
Hexamer	31.33	24.05	27.69	4.56	30.95	23.56	27.25	4.97
Heptamer	30.55	25.21	27.88	4.37	30.14	24.67	27.41	4.81
Octamer	30.87	23.08*	27.11	5.14	30.56	22.35*	26.56	5.66
		27.26•				26.67•		
		27.26§				26.67§		
Dodecamer	30.89	22.35*	26.73	5.52	30.61	21.78*	26.23	5.99
		26.30•				25.80•		
		27.40§				26.72§		

[a] $\sigma_H^{(f)}$ and $\sigma_H^{(h)}$ – the average of the magnetic shielding constants of free and hydrogen bonded protons, respectively; σ_H – the overall average of the proton magnetic shielding constant.

[b] $\sigma_H^{TMS} = 32.25$ ppm

[c] $\sigma_H^{TMS} = 32.22$ ppm

*,§,•See text and footnotes of Table 2 of ref. [11]

All water clusters contain both free and hydrogen bonded hydroxyl protons. In addition, the spatial clusters – i.e. octamer ≡ (tetramer)₂ and dodecamer ≡ (hexamer)₂ – contain three types of hydrogen bonded protons: two of them are within tetramer and hexamer planes; the third is located between planes. We denote them as *, • and § in Table 1 (this is consistent with notation used in ref. [11]); they have, in general, different magnetic shielding constants. In the case of methanol clusters only linear structures contain free hydroxyl protons. These are (in addition to monomer): dimer and one of pentamers (see ref. [11]). Clusters are in *dynamical* equilibrium in the bulk phase. It is likely that only the average of magnetic shielding constants of both free and hydrogen bonded protons is observed in experiment.

Table 2: The average SCF/GIAO ¹H isotropic magnetic shielding constants[a] and chemical shifts δ (relative to TMS) in methanol clusters (in ppm) calculated at DFT/B3LYP/6-311G(d,p) optimized geometries.

| Structure | SCF/GIAO/6-311G(d,p)[b] | | | | | | SCF/GIAO/6-311++G(d,p)[c] | | | | | |
| | $-OH$ | | | | $-CH_3$ | | $-OH$ | | | | $-CH_3$ | |
	$\sigma_H^{(f)}$	$\sigma_H^{(h)}$	σ_H	δ	σ_H	δ	$\sigma_H^{(f)}$	$\sigma_H^{(h)}$	σ_H	δ	σ_H	δ
Monomer	32.33		32.33	−0.08	28.97	3.28	32.18		32.18	0.04	28.94	3.28
Dimer	31.82	28.78	30.30	1.95	28.99	3.26	31.65	28.44	30.04	2.18	28.94	3.28
Trimer		28.01	28.01	4.24	29.06	3.19		27.50	27.50	4.72	29.01	3.21
Tetramer		26.09	26.09	6.16	29.09	3.16		25.57	25.57	6.65	29.03	3.19
Pentamer-1	31.87	26.21	27.35	4.90	29.00	3.25	31.65	25.79	26.96	5.26	28.92	3.30
Pentamer-2		25.30	25.30	6.95	29.09	3.16		24.84	24.84	7.38	29.03	3.19
Hexamer-1		25.23	25.23	7.02	29.09	3.16		24.80	24.80	7.42	29.02	3.20
Hexamer-2		24.91	24.91	7.34	29.10	3.15		24.50	24.50	7.72	29.04	3.18
Heptamer		24.90	24.90	7.35	29.09	3.16		24.52	24.52	7.70	29.02	3.20

[a] $\sigma_H^{(f)}$ and $\sigma_H^{(h)}$ – the average magnetic shielding constants of free and hydrogen bonded protons respectively; σ_H – the average magnetic shielding constant.
[b] $\sigma_H^{TMS} = 32.25$ ppm.
[c] $\sigma_H^{TMS} = 32.22$ ppm.

The necessity of using diffuse functions for the proper description of shielding effects in hydrogen bonded clusters was already emphasized [3,6,20]. Upon incorporating diffuse functions to the basis set, magnetic shielding constants of hydroxyl protons in water clusters decreases by 0.2–0.4 ppm in the case of free, and 0.4–0.7 ppm in the case of hydrogen bonded protons (Table 1). Somewhat smaller effect is observed in methanol clusters: up to 0.2 ppm for free, and up to 0.5 ppm for hydrogen bonded protons (Table 2). It should be noted, that inaccuracy in the determination of the shielding constants in hydrogen bonded clusters due to the basis set incompleteness usually increases with a cluster size (see also ref. [3]). This often makes the theoretical investigations of the NMR spectra of hydrogen bonded liquids impractical, since any extension of a basis set significantly increases the timing of SCF/GIAO calculations.

Shielding of free hydroxyl protons in water clusters does not vary much with cluster size – the largest difference in the average magnetic shielding constant $\sigma_H^{(f)}$ among clusters is equal to about 0.5 ppm. The only exception is the cyclic heptamer for which it is close to 1 ppm. However, its structure is irregular (see Figure 1h of ref. [11]) – a few of free protons exhibit residual hydrogen bond interactions within the 7–membered ring. Much larger difference is observed for the hydrogen bonded protons. With an increasing cluster size the magnetic shielding constant $\sigma_H^{(h)}$ calculated with 6-311++G(d,p) basis set changes: from 27.82 ppm for dimer down to 21.78 ppm for dodecamer. Similar effect is observed in the case of methanol. The magnetic shielding constant of free protons in linear dimer and pentamer remain close to that of monomer. With an increasing cluster size the decrease of $\sigma_H^{(h)}$ by as much as $\approx$ ppm (i.e. from 28.44 ppm for dimer down to 24.52 ppm for heptamer) is observed. On the other hand the average magnetic shielding constant of protons in the methyl groups of methanol clusters remain practically unchanged.

The average values of the magnetic shielding constants σ_H of *all* hydroxyl protons (i.e. free and hydrogen bonded) in water and methanol clusters are plotted *vs.* cluster size in Figures 1 and 2. The asymptotic behaviour of σ_H is observed; the limits for 6-311++G(d,p) basis set are: $\lim_{n\to\infty}\sigma_H \approx 26$ ppm for water and $\lim_{n\to\infty}\sigma_H \approx 24.5$ ppm for methanol. In addition to magnetic shielding constants the chemical shifts of protons relative to TMS were calculated. Their values are reported in Tables 1 and 2. The downfield migration of hydroxyl proton signal for water (by ≈ 5 ppm) and methanol (by ≈ 7.5 ppm) with an increasing cluster size – similar to the one reported for ethanol clusters [2,3] – is observed. Note that all water clusters contain strongly shielded free

hydroxyl protons – they should therefore exhibit smaller decrease in the magnetic shielding constants than alcohol clusters.
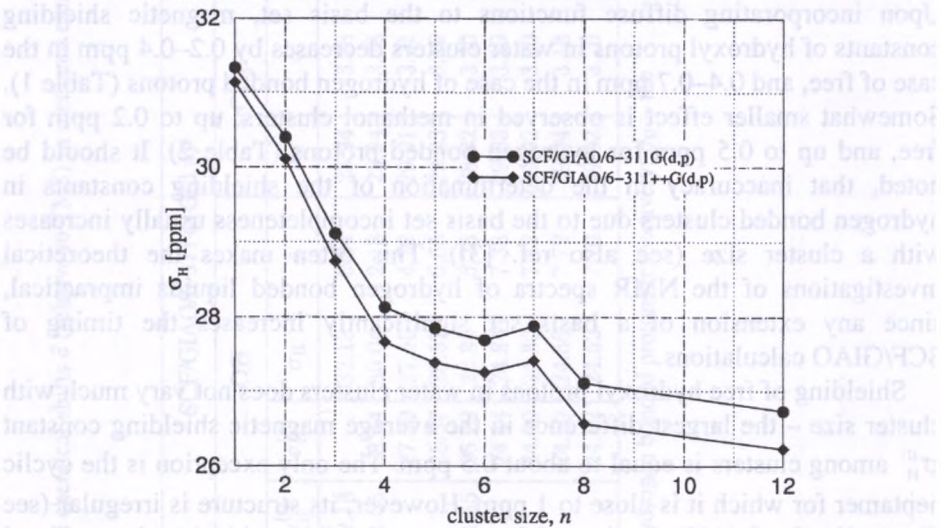

Fig. 1. SCF/GIAO/6-311G(d,p) and SCF/GIAO/6-311++G(d,p) hydroxyl proton magnetic shield ing constants of water clusters as a function of a cluster size
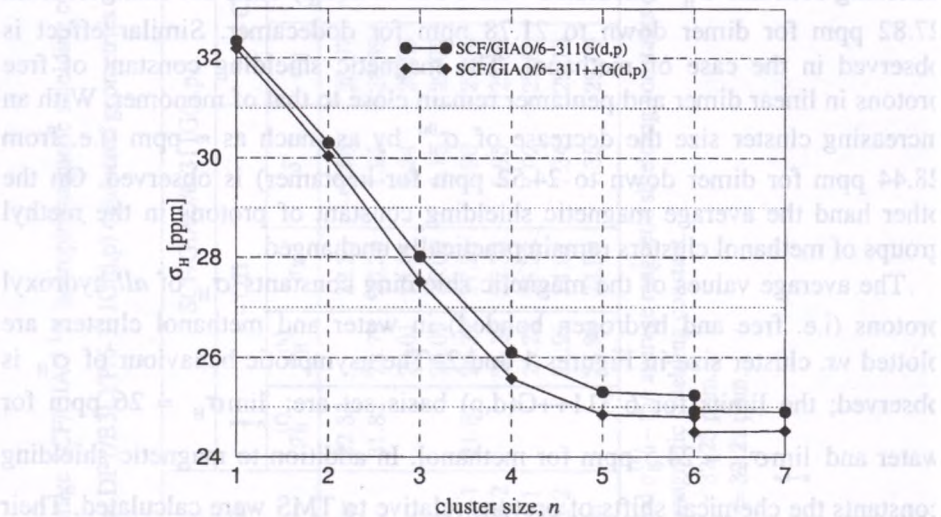

Fig. 2. SCF/GIAO/6-311G(d,p) and SCF/GIAO/6-311++G(d,p) hydroxyl proton magnetic shielding constants of methanol clusters as a function of a cluster size. The magnetic shielding constants of high-energy linear pentamer are not plotted. Two values for $n = 6$ correspond to two enegetically close conformations of methanol hexamer clusters
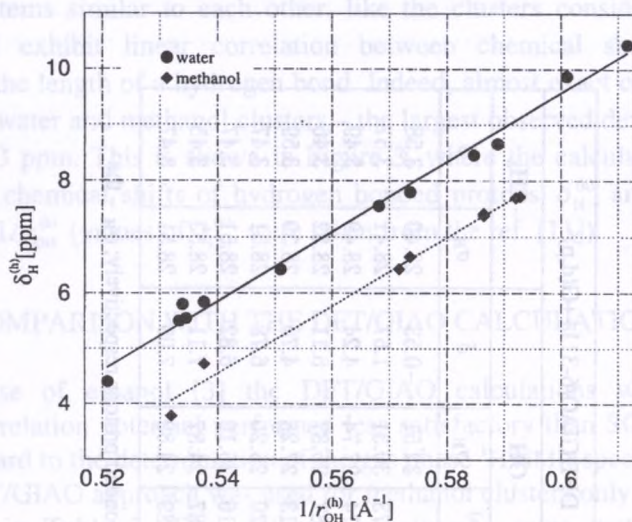
Fig. 3. Chemical shifts of hydrogen bonded hydroxyl protons of water and methanol clusters plotted against $1/r_{OH}^{(h)}$

It is evident, that any change in the populations of clusters in the bulk phase (due to the change of temperature, concentration, etc.) should alter the location of OH proton signal. On the other hand the chemical shifts of methyl protons in methanol clusters do not change with cluster size – as in ethanol the location of the CH_3 proton signal should be unaltered by the change of temperature. Note, that the chemical shift of the methyl protons in methanol is close to the chemical shift of the methylene protons in ethanol (compare Figure 2 of ref. [3]). It is thus the neighbourhood of hydroxyl group that is responsible for the changes in shielding of bonded to carbon protons.

Magnetic properties of molecules are closely related to their geometry. In particular, the chemical shifts of hydrogen bonded protons were shown to be roughly proportional to the reciprocal of the length of a hydrogen bond $r_{OH}^{(h)}$ [21]. This effect was shown to arise mostly from polarization of the OH bond in the presence of proton acceptor. Experimental data for a number of substances were used to show this correlation. However, deviations from the linear relation as large as a few ppm were observed. They are most likely due to other than polarization mechanisms responsible for the change in the chemical shifts for a given hydrogen bonded system. Therefore in our opinion it is not well justified   to correlate chemical shifts with $1/r_{OH}^{(h)}$ for chemically different species.

Table 3. The average DFT/GIAO ^{1}H isotropic magnetic shielding constants[a] and chemical shifts δ (relative to TMS) in methanol clusters (in ppm) calculated at DFT/B3LYP/6-311G(d,p) optimized geometries

| Structure | DFT/GIAO/6-311G(d,p)[b] | | | | | | DFT/GIAO/6-311++G(d,p)[c] | | | | | |
| | -OH | | | | -CH$_3$ | | -OH | | | | -CH$_3$ | |
	$\sigma_H^{(f)}$	$\sigma_H^{(h)}$	σ_H	δ	σ_H	δ	$\sigma_H^{(f)}$	$\sigma_H^{(h)}$	σ_H	δ	σ_H	δ
Monomer	32.70	32.70	32.70	-0.69	28.46	3.55	32.51		32.51	-0.53	28.40	3.58
Dimer	32.10	29.15	30.63	1.38	28.50	3.51	31.89	28.73	30.31	1.67	28.41	3.57
Trimer		28.41	28.41	3.60	28.59	3.42		27.74	27.74	4.24	28.49	3.49
Tetramer		26.55	26.55	5.46	28.64	3.37		25.87	25.87	6.11	28.52	3.46
Pentamer-1	32.13	26.66	27.76	4.25	28.53	3.48	31.85	26.13	27.28	4.70	28.39	3.59
Pentamer-2		25.79	25.79	6.22	28.62	3.39		25.20	25.20	6.78	28.51	3.47
Hexamer-1		25.70	25.70	6.31	28.62	3.39		25.16	25.16	6.82	28.51	3.47
Hexamer-2		25.39	25.39	6.62	28.63	3.38		24.87	24.87	7.11	28.53	3.45
Heptamer		25.36	25.36	6.65	28.61	3.40		24.89	24.89	7.09	28.51	3.47

[a] $\sigma_H^{(f)}$ and $\sigma_H^{(h)}$ – the average magnetic shielding constants of free and hydrogen bonded protons respectively; σ_H – the average magnetic shielding constant.
[b] σ_H^{TMS} = 32.01 ppm.
[c] σ_H^{TMS} = 31.98 ppm.

However, systems similar to each other, like the clusters considered in this work, should exhibit linear correlation between chemical shift and the reciprocal of the length of a hydrogen bond. Indeed, almost exact correlation is held for both water and methanol clusters – the largest observed deviation from linearity is 0.3 ppm. This is shown in Figure 3, where the calculated average values of the chemical shifts of hydrogen bonded protons $\delta_H^{(h)}$ are plotted as a function of $1/r_{OH}^{(h)}$ (values of $r_{OH}^{(h)}$ were taken from the ref. [11]).

4. COMPARISON WITH THE DFT/GIAO CALCULATIONS

In the case of ethanol [3] the DFT/GIAO calculations with B3LYP exchange–correlation potential performed less satisfactory than SCF/GIAO, at least with regard to the determination of the gas phase ^{1}H NMR spectrum. In this work the DFT/GIAO approach was used for methanol clusters only. The results are reported in Table 3. They follow basically the same patterns as the SCF/GIAO results: the downfield migration of the hydroxyl proton signal, no change in the shielding of methyl protons, etc. with increasing cluster size. However, it is hard to judge at this stage which of the approaches (SCF/GIAO or DFT/GIAO) predicts better ^{1}H NMR spectrum of liquid water and methanol. For that purpose the population weighted chemical shifts should be compared to experimental spectrum. This problem will be addressed in the nearest future.

It should be also noted that our SCF/GIAO calculations for water dimer are consistent with reported recently [6]. However, there are small differences in both magnetic shielding constant and its change upon the hydrogen bond formation between our values and those of the reference [6]. They can be attributed to the difference in the molecular geometry used in both calculations.

5. CONCLUSIONS

We calculated magnetic shielding constants of water and methanol clusters at the SCF/GIAO level of theory with two basis sets: 6-311G(d,p) and 6-311++G(d,p). The presence of diffuse functions in the basis set was confirmed to be essential for accurate calculations of the magnetic shielding constants. The downfield migration of the hydroxyl proton chemical shift with increasing cluster size is predicted for both systems. These changes are large – they amount to: $\approx$ 4 ppm for water and $\approx$ 7.5 ppm for methanol going from monomer to higher clusters. Smaller decrease of the chemical shift for water clusters compared to methanol is due to the presence of strongly shielded, free hydroxyl protons in all water clusters. The reported calculations indicate, that there should be profound changes in the location of the hydroxyl proton signal

with temperature in ^{1}H NMR spectrum: the higher the temperature the smaller clusters should be favoured in the liquid phase – the hydroxyl proton ^{1}H NMR signal should move up field.

In addition almost exact linear correlation between the chemical shift and reciprocal of the length of a hydrogen bond is observed for both water and methanol clusters.

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