Ab Initio NMR Study of the Isomeric Hydrogen-Bonded Methanol–Water Complexes

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ABSTRACT: Isotropic and anisotropic chemical shifts for all atoms of complexes $CH_3HO \cdots H_2O$ and $CH_3OH \cdots OH_2$ have been calculated at the Hartree–Fock, second-order Møller-Plesset (MP2) and density functional (B3LYP) theoretical levels using the 6-311++G(2*d*,2*p*) basis set. The influence of the hydrogen bond formation on the nuclear magnetic resonance chemical shifts in all atoms is analyzed. The basis set superposition error was taken into account, and its effects were more significant for the anisotropic shieldings on the oxygen atoms of the proton donor $CH_3OH \cdots OH_2$ and proton acceptor methanol $CH_3HO \cdots H_2O$. Using counterpoise correction to the MP2 results, our best estimate for the calculated isotropic and anisotropic shifts of the H atom involved in the hydrogen bond are −2.98 and 11.95 ppm for $CH_3HO \cdots H_2O$ and −2.91 and 11.48 ppm for the $CH_3OH \cdots OH_2$ isomer, respectively. For the O atom of the OH hydrogen bonded, these calculated shifts are −5.21 and −5.35 ppm for $CH_3HO \cdots H_2O$ and −6.32 and −8.75 ppm for $CH_3OH \cdots OH_2$. The effect of monomer relaxation was also considered and was found to be appreciable only for the oxygen atom of the proton donor OH due to the distance increase after complex formation.

Key words: NMR; methanol–water; hydrogen bond; chemical shift; ab initio

Introduction

Water–alcohol mixtures exhibit anomalous behavior compared with the properties of the pure components. When alcohol and water are mixed, the entropy of the mixture increases less than expected. This effect was first pointed out by Frank and Evans [1] and was explained in terms of a hydrophobic interaction with the nonpolar alcohol headgroups, which induces an ice-like structure in the surrounding water. There is extensive literature on this topic [2–12]. Spectroscopic studies [2–9] and computer simulations [8, 10–12] have been performed to study the structure of water–alcohol mix-

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tures. Early neutron diffraction studies provided structural information about water cages around hydrophobic headgroups in solution [2, 5]. More recently, a neutron diffraction study demonstrated that incomplete mixing at the molecular level is essential to explain the "smaller than expected" entropy increase observed when methanol dissolves in water [8]. A recent study of x-ray emission spectroscopy provided a description of the details of the incomplete mixture at the molecular level [9].

An important aspect that is crucial to the interpretation of the alcohol–water structure is the network of hydrogen bonds that is formed. To rationalize the local structure of the incomplete mixture at the molecular level, it is important to understand this molecular interaction. Thus, the study of the hydrogen-bonded complexes of alcohol–water mixtures can be important to characterize this local structure even in the cluster situation. Beyond this specific aspect, methanol–water complexes are good models to understand the behavior of the hydrogen bond (O—H $\cdots$ O) because, like water, methanol is both proton acceptor ($CH_3HO \cdots H_2O$) and proton donor ($CH_3OH \cdots OH_2$). It was recently established that these two methanol–water complexes have equivalent binding energies [13–15], even in the liquid case [16].

An important spectroscopic technique that has been employed in hydrogen bond investigation is nuclear magnetic resonance (NMR). However, few NMR studies of alcohol–water have been carried out. In an experimental work, Ludwig [17] studied NMR relaxation in alcohol–water mixtures, showing that the reorientational correlation time and the quadrupole coupling constants of water are very sensitive on the concentration of solute. In another work, the behavior of hydrogen bond with temperature has been analyzed by ab initio calculations of liquid alcohols [18]. The magnetic properties such as the isotropic and anisotropic chemical shifts have been used to detect and characterize hydrogen bonds. These applications began about 50 years ago with experiments on the effects of temperature and solvent on the OH proton chemical shift of ethanol [19]. Many researchers have determined the proton chemical shift in liquid and gas phases for several hydrogen-bonded systems, such as hydrides [20], alcohols [21], phenols [22], carboxylic acids [22], peptides [23], amides, and proteins [24, 25]. In a study on water, Ditchfield [26–28] observed that the proton anisotropic chemical shielding was more sensitive to the presence of hydrogen bond than the isotropic chemical shielding value. In other studies,

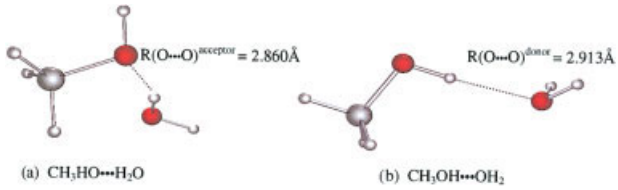

FIGURE 1. MP2/6-311++G(2*d*,2*p*) optimized methanol–water complexes used in the NMR calculations and the R_{OO} distance. (a) Methanol as proton acceptor. (b) Methanol as proton donor.

Ditchfield and colleagues [29, 30] pointed out that the components of the chemical shielding tensor in the proton donor, which are perpendicular to the hydrogen bond axis, are more sensitive to the formation of a hydrogen bond than the parallel component. Many theoretical studies have been published from then on and shown their reliability in understanding experimental data. Hinton and Wolinski [31] reviewed the main applications of ab initio calculations on systems that present hydrogen bonds.

The hydrogen bonds of methanol–water complexes are studied in this article using ab initio calculated NMR parameters. A description of the chemical environment of each nucleus of the complexes is given to verify the relative effects on the nucleus that participates in the hydrogen bond. For this, the isotropic (δ^{iso}) and anisotropic (δ^{anis}) chemical shifts are analyzed as well as the parallel ($\delta_{\|}$) and perpendicular ($\delta_{\perp}$) components of the chemical shift tensor in relation to the hydrogen bond axis.

Calculation Details

The second-order Møller-Plesset (MP2) has proved a good theoretical model for the study of hydrogen-bonded clusters. The MP2 approach is known to provide molecular geometries with accuracy and reliability [32]. Thus, MP2/6-311++G(2*d*,2*p*) calculations were performed to obtain the geometries of the complexes $CH_3HO \cdots H_2O$ and $CH_3OH \cdots OH_2$, as well as the isolated species (monomers) CH_3OH and H_2O. Figure 1(a) and (b) shows the optimized complexes in which the methanol molecule is the proton acceptor and the proton donor, respectively. NMR constants were calculated for these complexes and the monomers from three different theoretical models using the gauge-including atomic orbital method (GIAO) [26–28]. First, we use the GIAO/Hartree–Fock self-consis-

tent field (SCF) [33] method. Electron correlation effects are then obtained using the second-order GIAO/MP2 level [34, 35]. For comparison, density functional theory (DFT) (GIAO/DFT) [36–38] was also used in the three-parameter exchange correlation functional of Becke–Lee–Yang and Parr (B3LYP). The use of these three theoretical levels aims at establishing the relative importance of electron correlation effects on the calculated NMR shieldings. In all cases, the extended 6-311++G(2*d*,2*p*) basis set was used since it has been demonstrated that basis sets at least as large as the 6-311++G(*d*,*p*) is needed to provide agreement with experiment [39, 40]. The basis set superposition error (BSSE) was corrected, using the counterpoise correction [41]. This was carried out for each complex by calculating the chemical shielding of the monomer in the presence of the basis functions of the complex. The effect of monomer relaxation was also considered. It was obtained as the difference between the shielding in the geometry of the complex and the shielding in the geometry of the monomer. All calculations were carried out with the Gaussian 98 package [42].

Results and Discussion

ABSOLUTE CHEMICAL SHIELDINGS

Figure 1 shows the calculated O···O distances for both complexes. The O···O distances for the complexes where the methanol molecule is the proton acceptor and proton donor are calculated as 2.860 Å and 2.913 Å, respectively. An early theoretical study by Kirschner and Woods [43] found the results of 2.845 Å and 2.912 Å, respectively, in good agreement with our results. The experimental result for the proton acceptor case has been inferred as 2.997 ± 0.009 Å [15], but this experimental value could not be reproduced theoretically, even at a very high level of calculation [43]. The influence of this difference between the theoretical and experimental O···O distances in the NMR parameters, for the proton acceptor case, has been analyzed and found to be small. For instance, at the B3LYP level, the differences in the calculated shieldings for the atoms involved in the hydrogen bond, the O atom of methanol and the H atom of water, are, respectively, 0.20 ppm and 0.74 ppm.

There are indications that for the NMR properties of larger molecules, it may be sufficient to carry out calculations at the DFT or even the SCF level [26, 39, 44, 45]. In general, correlation effects are important [46]. In calculations of the absolute chemical shielding, it is important to include electron correlation effects in a more controllable manner than is usually the case in molecular DFT calculations. Therefore, all calculations are made at the MP2 level, but the results are also given for the case of B3LYP and SCF, for comparison. The calculated absolute isotropic and chemical anisotropic shieldings for the isolated species, methanol and water, are shown in Table I. We report the values determined using the three theoretical methods considered here, but in every case the geometry used is that obtained at the MP2/6-311++G(2*d*,2*p*) level. All values for the isotropic shieldings are in relatively good agreement with the respective experimental result. We can observe that the MP2 results are in reasonable agreement with experiment for the isotropic shielding of all atoms in the methanol molecule. This result is improved in the case of water. Interestingly, the electron correlation obtained at the B3LYP level has an opposite sign with respect to the MP2 results. For instance, the isotropic shielding for the O atom of methanol using B3LYP is smaller than the SCF value showing that electron correlation decreases this shielding. This is in contrast to what has been obtained at the MP2 level, where the electron correlation effects at the second-order increase the shielding, improving the theoretical result. Comparing the SCF and MP2 results for the isotropic shielding, we note that electron correlation effects increase the values of the isotropic shielding of the oxygen atom by ~13 ppm.

A proper comparison between MP2 and DFT requires reliable experimental results for reference. The experimental values of the isotropic chemical shielding of the oxygen atom of water has been established earlier [58] to be 344.0 ppm in very good agreement with our MP2 result of 344.8 ppm, as shown in Table I. This would imply poor performance of the B3LYP model. However, this value has recently been revisited [59], and the value of 323.6 ppm has been suggested. This now reverses the agreement showing the excellent performance of the B3LYP model and an overestimation by the MP2. This final value for the oxygen atom of the water molecule is in line with the current view that MP2 tends to overestimate isotropic shieldings [49–51]. However, attention is now paid to the vibration contribution, not accounted for in our calculations. Although this is not very important in chemical shifts, because they tend to cancel, the present discussion refers to the absolute shielding. This vibration contribution has been estimated as −12 ppm

TABLE I

Values of the isotropic and anisotropic chemical shieldings of methanol and water (in ppm), using three theoretical levels.*

	Isotropic chemical shielding (σ^{iso})			
	SCF	B3LYP	MP2	Exp
CH_3OH				
O	337.77	321.65	350.47	345.9[a]
C	145.52	130.22	144.37	136.6[b]
H	28.88	28.21	28.27	27.34[c]
H	28.88	28.21	28.27	27.34[c]
H	28.90	28.43	28.42	27.34[c]
H_o	31.98	32.33	31.99	30.73[c]
H_2O				
H	30.86	31.45	30.99	30.09,[c] 30.05[i]
O	327.08	326.36	344.78	344.0,[d] 323.6[h]
H	30.86	31.45	30.99	30.09,[c] 30.05[i]
	Anisotropic chemical shielding (σ^{anis})			
	SCF	B3LYP	MP2	Others
O	97.57	95.90	90.96	96.9[e]
C	67.92	80.54	77.97	63.8[e]
H	8.30	8.26	8.61	7.83[f]
H	8.30	8.26	8.61	7.83[f]
H	7.76	7.28	7.68	7.63[f]
H_o	20.40	18.11	19.72	—
H_2O				
H	20.41	19.18	20.35	20.39,[g] 19.10[j]
O	56.49	54.05	46.03	46.05,[g] 46.97[j]
H	20.41	19.18	20.35	20.39,[g] 19.10[j]

* The fourth column presents the experimental results for the isotropic shielding and other theoretical results for the anisotropic shielding.
[a] Liquid phase data cited by Kitzinger converted to an absolute [55].
[b] Ref. [56].
[c] Ref. [57].
[d] Ref. [58].
[e] Ref. [44].
[f] Calculated for methyl group in methylformate Ref. [48].
[g] Ref. [51].
[h] Ref. [59].
[i] Ref. [60].
[j] Ref. [61].

for the oxygen chemical shielding of water [52, 53]. If that is considered now, the MP2 result is again more realistic. The same reasoning appears to apply to the anisotropic shieldings. Recent theoretical values for water obtained by Helgaker and coworkers [61], using elaborated multiconfigurational calculations, confirmed the value for the oxygen atom of the water molecule close to 46.97 ppm, in good agreement with our MP2 results, but suggested a value of 19.10 ppm for the hydrogen atoms, now in better comparison with our B3LYP results.

For the methyl hydrogen atoms, as well as the carbon atom of the methanol molecule, the electron correlation effects decrease the isotropic shielding by a relatively mild value, ~0.5–1.0 ppm. For the anisotropic shielding (bottom section of Table I), a more compatible picture emerges regarding the effects of electron correlation. In this case, B3LYP and MP2 have the same trend with respect to the results at the SCF level. Again, this agreement is improved in the case of the water molecule. The theoretical results for the anisotropic shielding can only be compared with other previous theoretical results and overall there is good agreement. As noted earlier [44], the effects of electron correlation are more pronounced for the heavy atoms (oxygen and carbon, this case). For water, the difference between the MP2 and the SCF results is 17.70 ppm in the case of the isotropic shielding of the oxygen atom and 10.05 ppm for the anisotropic shielding of the carbon atom. The previous methanol values [44, 48] shown in Table I for the anisotropic case were obtained at the SCF level and, as can be seen, they are in better agreement with our SCF results. A systematic study of NMR parameters for acyclic and isolated alcohols at a lower DFT level has been presented [62]. Electron correlation, however, makes a difference, for instance, decreasing the O value (by 6.61 ppm) and increasing the C value (by 10.05 ppm). A previous theoretical result for water, using the MP2 method with the all-electron correlation, obtained [51] results in very good agreement with our present results (Table I) using the frozen core approximation, indicating that inner orbitals do not make a difference in these calculated NMR shieldings. Overall, MP2 appears to be a more consistent model for obtaining the absolute chemical shieldings of methanol and water.

CHARGE REARRANGEMENTS

Upon formation of a hydrogen bond, there is a charge rearrangement with a slight increase in the electron density in the proton acceptor site and a slight decrease in the hydrogen-bonded proton. Normally there is also an increase of the electron density in the donor O atom due to charge transfer and a loss of electron density in the hydrogen-

TABLE II

Variation in the Mulliken atomic charge (in elementary units) on the atoms of $CH_3HO \cdots H_2O$ and $CH_3OH \cdots OH_2$ complexes.

		Difference in the charge	
	Monomers	$CH_3OH \cdots OH_2$	$CH_3HO \cdots H_2O$
H_2O			
H	0.24	0.02	0.07
O	−0.48	−0.05	−0.07
H	0.24	0.02	0.00
CH_3OH			
O	−0.48	−0.09	−0.05
C	0.13	0.00	−0.01
H	0.03	0.00	0.01
H	0.03	0.00	0.02
H	0.05	−0.01	0.01
H	0.24	0.11	0.02

bonded proton. These charge rearrangements affect the chemical shifts and help understanding the calculated shifts that are discussed next. Of course, charge densities are not true physical observables and the Mulliken population analysis suffer from basis set and other dependencies. Thus, presenting these charge density results has the only interest of a qualitative comparison of charge rearrangements and chemical shifts. Table II thus presents the Mulliken charge density on the atoms of the monomers and the variation of these charges upon complexation. We can observe that the O atom as a bond acceptor accumulates a charge of the $-0.05e$ in both water and methanol molecules, whereas in the hydrogen-bonded proton there is a decrease of charge of $0.07e$ and an increase of $0.11e$ in the water and methanol molecules, respectively. At the O atom of the OH proton donor, the increase of electron density is $-0.09e$ and $-0.07e$, for the methanol and water molecules, respectively.

CHEMICAL SHIFTS

The isotropic and anisotropic chemical shifts for atom X are calculated as

$$\delta(X)^{\text{iso}} = \sigma(X)^{\text{iso}}_{\text{cluster}} - \sigma(X)^{\text{iso}}_{\text{monomer}} \quad (1)$$

and

$$\delta(X)^{\text{anis}} = \sigma(X)^{\text{anis}}_{\text{cluster}} - \sigma(X)^{\text{anis}}_{\text{monomer}} \quad (2)$$

where the isotropic shielding is obtained as

$$\sigma^{\text{iso}} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (3)$$

and the isotropic shielding as

$$\sigma^{\text{anis}} = \sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22}) \text{ with } \sigma_{11} < \sigma_{22} < \sigma_{33}. \quad (4)$$

σ_{11}, σ_{22}, and σ_{33}, are the principal values of the σ tensor. In experimental NMR spectra, a standard system is chosen as reference. Thus, the chemical shift is taken as the difference between the shielding of the atom in the system and in the reference. Using the same reference system, the calculated chemical shift for the isolated and the complex systems corresponds to the difference in the two situations as the shielding for the reference system cancels out. Hence, the chemical shifts reported refer to the difference between the shielding of the atom in the complex and the shielding of this same atom in the monomer.

All results for the isotropic and anisotropic chemical shifts were corrected for BSSE using the counterpoise correction [41], where for each complex, we also calculated the shielding of the monomer using the entire basis functions of the hydrogen-bonded complex. The uncorrected (without CC) and corrected (with CC) results for BSSE are shown at Tables III and IV and are discussed below.

Methanol as Proton Acceptor–$CH_3HO \cdots H_2O$ Complex

Table III shows the results for the δ^{iso} and δ^{anis} for the $CH_3HO \cdots H_2O$ complex. We first consider the atoms involved in the hydrogen bond. In the methanol molecule, the calculated δ^{iso}(O) are −3.78, −5.85, and −5.21 ppm and in the water molecule, δ^{iso}(H) are −3.14, −3.18, and −2.98 ppm in the SCF, B3LYP, and MP2 methods, respectively. For the other atoms of the complex, the δ^{iso} is small, but for the oxygen atom of the water molecule, it is −0.84 ppm (using MP2) because of the modification that the structure of water undergoes upon complexation. The counterpoise correction to BSSE is relatively mild but can be more pronounced for the O atom of water with a relative importance of the electron correlation effects. It is expected that, upon complex-

TABLE III

Values of the isotropic and anisotropic chemical shifts for the $CH_3HO \cdots H_2O$ complex (in ppm), using three theoretical models.

	Isotropic chemical shift (δ^{iso})					
	SCF		B3LYP		MP2	
$CH_3HO \cdots H_2O$	Without CC	With CC	Without CC	With CC	Without CC	With CC
O[a]	−4.81	−3.78	−6.96	−5.85	−5.95	−5.21
C	−0.58	−0.08	−0.42	0.06	−0.50	−0.02
H	−0.07	−0.04	0.02	0.05	−0.02	0.01
H	−0.14	−0.13	−0.06	−0.06	−0.08	−0.07
H	−0.14	−0.13	−0.11	−0.12	−0.11	−0.11
H_o	−0.52	−0.48	−0.62	−0.58	−0.56	−0.51
H[a]	−3.50	−3.14	−3.51	−3.18	−3.34	−2.98
O	0.98	2.97	−1.52	0.23	−1.81	−0.84
H	0.54	0.57	0.50	0.54	0.43	0.47
	Anisotropic chemical shift (δ^{anis})					
	SCF		B3LYP		MP2	
$CH_3HO \cdots H_2O$	Without CC	With CC	Without CC	With CC	Without CC	With CC
O[a]	−7.11	−5.69	−9.35	−7.51	−6.77	−5.35
C	0.72	0.15	0.47	−0.07	0.71	0.18
H	0.51	0.53	0.33	0.33	0.44	0.45
H	−0.05	0.02	−0.04	0.03	−0.07	0.01
H	−0.22	−0.15	−0.11	−0.02	−0.18	−0.10
H_o	0.19	0.26	0.12	0.21	0.15	0.23
H[a]	11.51	11.90	11.58	12.00	11.53	11.95
O	8.22	6.67	11.24	9.40	11.50	9.31
H	0.41	0.54	0.25	0.42	0.26	0.39

CC, counterpoise correction.

[a] Atom directly involved in the hydrogen bond.

ation, there is a charge redistribution in the O—H bond (0.07*e* at H and −0.07*e* at O), leading to a more appreciable shift. Overall, the three theoretical methods give similar and consistent results for the isotropic shift.

The δ^{anis} for the same complex are more pronounced; i.e., −5.69, −7.51, and −5.35 ppm for the oxygen atom and 11.90, 12.00, and 11.95 ppm for the hydrogen atom in the hydrogen bond. Again, for the O atom of the water molecule, the δ^{anis}(O) is greatly influenced by electron correlation effects. The difference between the SCF and MP2 counterpoise corrected values is 2.64 ppm (6.67 and 9.31 ppm). Counterpoise correction affects the results by only 1.5–2.2 ppm, and in some cases it is negligible.

Methanol as Proton Donor–$CH_3OH \cdots OH_2$ Complex

A similar analysis is made in Table IV for the $CH_3OH \cdots OH_2$ complex. In this case, the δ^{iso}(O) of the oxygen atom of methanol are all positive, as compared with the $CH_3HO \cdots H_2O$ complex. For this O atom, the counterpoise corrected δ^{iso}(O) are 7.11, 4.85, and 2.81 ppm whereas the counterpoise corrected δ^{anis}(O) are −13.24, −10.54, and −5.85 ppm with the three theoretical models. Note that in this complex the BSSE is larger. For instance, the calculated δ^{anis}(O) of the methanol and water molecules change from −1.40 to −5.85 ppm (methanol) and from −6.93 to −8.75 ppm (water). For the hydrogen atom of methanol that is the proton donor, the calculated δ^{iso}(H) are, respectively, −3.05,

TABLE IV

Values of the isotropic and anisotropic chemical shifts for $CH_3OH \cdots OH_2$ complex (in ppm), using three theoretical models.

	Isotropic chemical shift (δ^{iso})					
	SCF		B3LYP		MP2	
$CH_3OH \cdots OH_2$	Without CC	With CC	Without CC	With CC	Without CC	With CC
O	5.37	7.11	3.11	4.85	1.66	2.81
C	1.23	1.03	1.23	1.08	1.06	0.88
H	0.10	0.11	0.08	0.09	0.06	0.08
H	0.10	0.11	0.08	0.09	0.06	0.08
H	0.14	0.14	0.09	0.10	0.08	0.09
H_o[a]	−3.33	−3.05	−3.35	−3.10	−3.17	−2.91
H	−0.55	−0.46	−0.60	−0.52	−0.57	−0.47
O[a]	−5.69	−5.31	−7.59	−7.57	−6.22	−6.32
H	−0.55	−0.46	−0.60	−0.52	−0.57	−0.47
	Anisotropic chemical shift (δ^{anis})					
	SCF		B3LYP		MP2	
$CH_3OH \cdots OH_2$	Without CC	With CC	Without CC	With CC	Without CC	With CC
O	−8.42	−13.24	−5.39	−10.54	−1.40	−5.85
C	−1.61	−1.40	−1.75	−1.51	−1.28	−1.16
H	0.19	0.17	0.34	0.32	0.25	0.23
H	0.19	0.17	0.34	0.32	0.25	0.23
H	0.52	0.52	0.48	0.49	0.52	0.52
H_o[a]	11.14	11.35	11.38	11.59	11.26	11.48
H	−0.02	0.08	−0.15	−0.03	−0.10	0.02
O[a]	−9.08	−9.85	−8.40	−10.19	−6.93	−8.75
H	−0.02	0.08	−0.15	−0.03	−0.10	0.02

CC, counterpoise correction.

[a] Atoms directly involved in the hydrogen bond.

−3.10, and −2.91 ppm. For the oxygen atom of water, the values of δ^{iso}(O) are all negative (−5.31, −7.57, and −6.32 ppm), as compared with the $CH_3HO \cdots H_2O$ complex. It is interesting to note here that δ^{iso}(C) = 0.88 ppm in MP2 is larger than the counterpart in the other complex (−0.02 ppm). This is possibly related to the larger amount of charge accumulated in the neighboring O atom (−0.09*e*) in comparison with the amount accumulated in the C atom in the other complex (0.05*e*).

There have been very few theoretical studies of NMR parameters of hydrogen-bonded water–methanol complexes. However, this isomer, the $CH_3OH \cdots OH_2$ complex, has been the subject of a previous study [54] in which some of the shielding constants were obtained using the MP2/aug-cc-pVTZ model without counterpoise correction. Overall, there is a good agreement between the results. It should be noted, however (Table IV), that in some cases the counterpoise correction is sizable (e.g., the δ^{anis} of the oxygen atom of the $CH_3OH \cdots OH_2$ complex).

The theoretical results for both complexes can be summarized pictorially in Figures 2 and 3. Figure 2 shows the δ^{iso} and δ^{anis} for each nucleus of the $CH_3OH \cdots OH_2$ complex, while Figure 3 shows the same results for the $CH_3HO \cdots H_2O$ complex. Figures 2 and 3 illustrate more clearly the chemical shifts after the hydrogen bond formation. We see that the C and H atoms of the methyl group present a small shift, while the atoms that participate in the hydrogen bond present a larger shift. From Figures 2 and 3, we can analyze the relative values of each theoretical method. We note that in the case of proton acceptor methanol, electron correlation is important for the isotropic shift of the oxygen atom of water. The SCF and B3LYP results are positive, whereas the MP2 method gives a negative value. For the

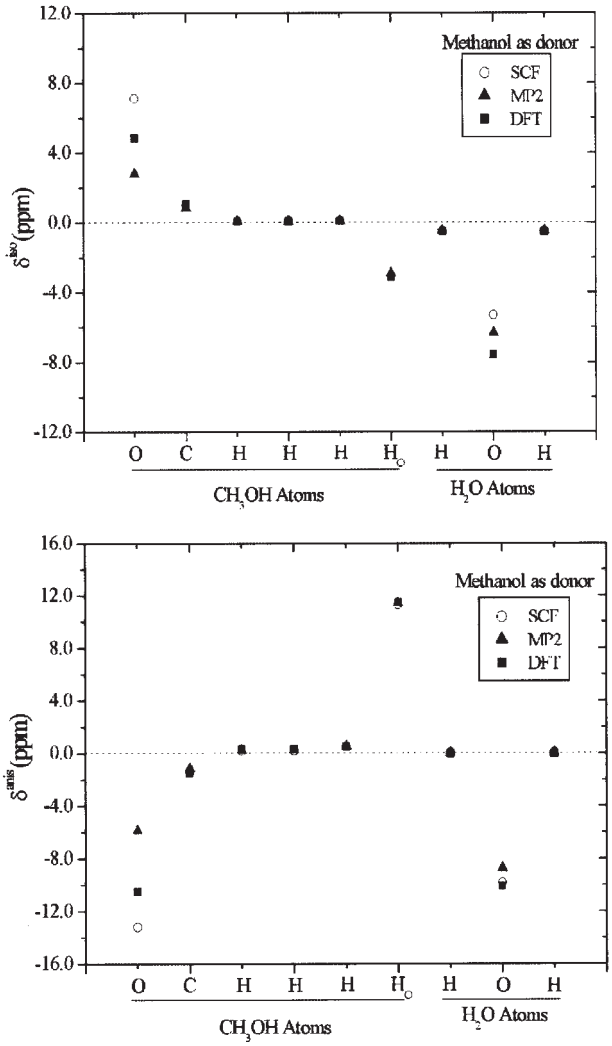

FIGURE 2. Isotropic and anisotropic chemical shifts for the $CH_3OH \cdots OH_2$ complex using three theoretical levels. Results corrected for BSSE.

hydrogen atoms of water, the electron correlation effects are small.

$\delta_\parallel$ AND $\delta_\perp$ COMPONENTS OF ISOTROPIC CHEMICAL SHIFT TENSOR

Experimentally, it is known that for the shielding tensor of the hydrogen-bonded proton, the most shielded direction is nearly parallel to the axis of hydrogen bond, whereas the least shielded is nearly perpendicular to this axis [30, 47]. It has been noted previously for the water dimer [29, 30] that these perpendicular components of the hydrogen-bonded proton chemical shielding tensor are more sensitive to the formation of a hydrogen bond than a parallel component. Although these parallel and perpendicular components are not independent from the previous results, it is of interest to analyze them separately. The parallel and perpendicular components for the atom X are defined as

$$\delta(X)_\parallel = \sigma(X)^{\text{iso}} + \frac{2}{3}\sigma(X)^{\text{anis}} \tag{5}$$

and

$$\delta(X)_\perp = \sigma(X)^{\text{iso}} - \frac{1}{3}\sigma(X)^{\text{anis}}. \tag{6}$$

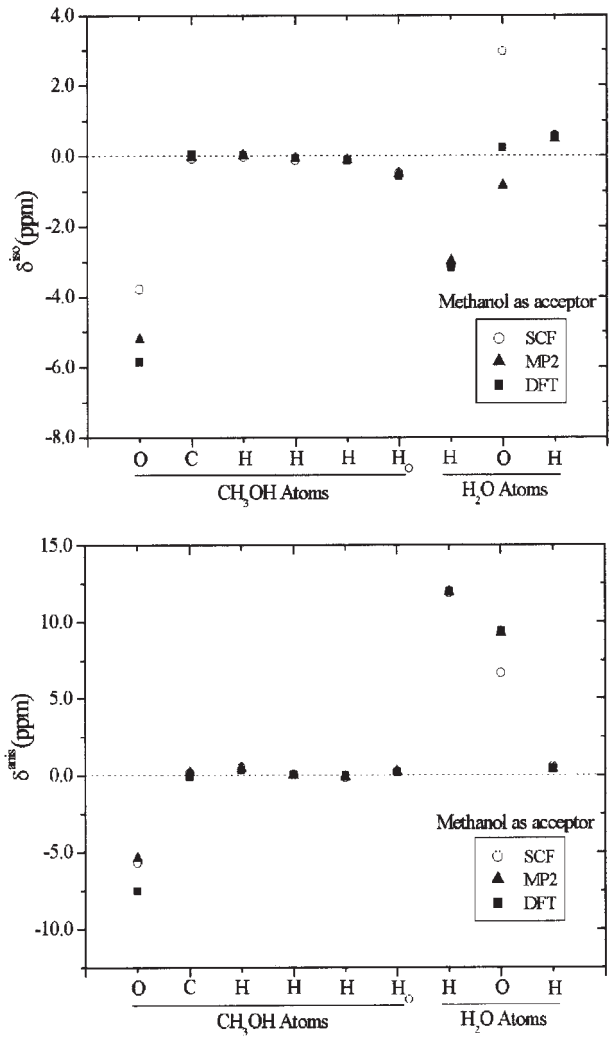

FIGURE 3. Isotropic and anisotropic chemical shifts for the $CH_3HO \cdots H_2O$ complex using three theoretical levels. Results corrected for BSSE.

TABLE V

Values of the parallel and perpendicular components of the isotropic shielding of $CH_3HO \cdots H_2O$ and $CH_3OH \cdots OH_2$ complexes (in ppm), using three theoretical models.

	$\delta_{\parallel}$			$\delta_{\perp}$		
$CH_3HO \cdots H_2O$	SCF	B3LYP	MP2	SCF	B3LYP	MP2
O[a]	−9.55	−13.20	−10.47	−2.44	−3.85	−3.70
C	−0.09	−0.10	−0.03	−0.82	−0.57	−0.73
H	0.27	0.24	0.27	−0.24	−0.09	−0.17
H	−0.18	−0.09	−0.13	−0.12	−0.05	−0.06
H	−0.29	−0.18	−0.23	−0.06	−0.07	−0.05
H_o	−0.39	−0.54	−0.46	−0.58	−0.66	−0.62
H[a]	4.17	4.21	4.35	−7.34	−7.37	−7.18
O	6.45	5.97	5.85	−1.76	−5.26	−5.65
H	0.81	0.66	0.61	0.41	0.41	0.34
$CH_3OH \cdots OH_2$	SCF	B3LYP	MP2	SCF	B3LYP	MP2
O	−0.24	−0.49	0.72	8.17	4.91	2.12
C	0.16	0.07	0.21	1.76	1.82	1.48
H	0.23	0.30	0.23	0.04	−0.03	−0.02
H	0.23	0.30	0.23	0.04	−0.03	−0.02
H	0.48	0.41	0.43	−0.04	−0.07	−0.10
H_o[a]	4.09	4.24	4.33	−7.04	−7.14	−6.93
H	−0.56	−0.70	−0.63	−0.54	−0.55	−0.53
O[a]	−11.74	−13.19	−10.84	−2.66	−4.79	−3.91
H	−0.56	−0.70	−0.63	−0.54	−0.55	−0.53

[a] Atom directly involved in the hydrogen bond.

Table V presents the values for the $\delta_{\parallel}$ and $\delta_{\perp}$ for all atoms of both complexes $CH_3HO \cdots H_2O$ and $CH_3OH \cdots OH_2$. For the $CH_3HO \cdots H_2O$ complex, $\delta_{\perp}$ is negative and generally larger (in absolute value) than the parallel component, except for the O atom of methanol and water. For instance, at the MP2 level, the calculated $\delta_{\perp}$(H) for the proton donor atom is −7.18 ppm, compared with the $\delta_{\parallel}$(H) value of 4.35 ppm (Table V). A similar result can be seen for the other complex $CH_3OH \cdots OH_2$. Now, again at the MP2 level, the $\delta_{\perp}$(H) of the proton donor atom is −6.93 ppm, compared with the $\delta_{\parallel}$(H) value of 4.33 ppm. However, it is also of interest to note the corresponding shifts in the proton acceptor oxygen atoms. The reverse occurs and the $\delta_{\parallel}$(O) is now dominant. Note, for instance, that the $\delta_{\parallel}$(O) of the O atom of methanol is −10.47 ppm and the O atom of water is −10.84 ppm, whereas the $\delta_{\perp}$(O) are −3.70 and −3.91 ppm, respectively. Also, they show the same sign (negative) for both complexes. Thus, we see that the perpendicular component of the isotropic shift tensor in the proton donor atom is larger in magnitude than the parallel component. However, this tendency is inverted for the oxygen atom of the hydrogen bond.

MONOMER RELAXATION EFFECT

It is now appropriate to comment on the separate effect of monomer geometry relaxation. This has been obtained in the present study as the difference between the shielding of the atom in the optimized geometry of the complex and the shielding of the same atom in the optimized geometry of the monomer. This difference was appreciable only for the oxygen atom of the proton donor molecule because of the O—H stretching upon hydrogen bond formation. In the case of the oxygen atom of proton donor methanol, it was 1.33 ppm (MP2) and 1.76 ppm (B3LYP) for the isotropic shielding and −4.62 ppm (MP2) and −5.38 ppm (B3LYP) for the anisotropic shielding. For the proton donor water molecule, the relaxation contributions are 1.70 ppm (MP2) and 2.18 ppm (B3LYP) ppm for the isotropic shielding and −0.16 ppm (MP2) and −0.41 ppm (B3LYP) for the anisotropic shielding.

Summary and Conclusions

In this work, we have analyzed the effects of hydrogen bond formation on NMR chemical shieldings for methanol–water complexes. Our purpose is to provide NMR data that could help understanding water–alcohol mixtures. This all-atom description of the chemical shift tensor in hydrogen-bonded complexes might be of value in understanding hydrogen bonds.

We have calculated NMR shieldings for all atoms in the two possible hydrogen bonded complexes, $CH_3HO \cdots H_2O$ and $CH_3OH \cdots OH_2$, using the SCF, B3LYP, and MP2 models in the MP2-optimized geometries. We obtained that the atoms of the methyl group present only very small isotropic chemical shifts, but the carbon atom of the donor methanol is more influenced. The results obtained for the isotropic (δ^{iso}) and anisotropic (δ^{anis}) chemical shifts are more sensitive for the atoms that participate directly in the hydrogen bond. The δ^{anis} appears to be a good indicator of the hydrogen binding since the anisotropic chemical shifts are larger than the corresponding isotropic one. These results corroborate previous assumptions that the δ^{anis}(H) are more sensitive than the isotropic shift [27, 28]. We also find that the atoms of the donor molecule become more shielded, while in the acceptor molecule the atoms become more deshielded. A similar tendency [44] have been observed in a study of the water dimer. Electron correlation effects were found to be important in the absolute chemical shielding, but not the chemical shifts. Whereas for the atoms that participate directly in the hydrogen bond the BSSE is numerically relevant, for the other atoms it is essentially negligible. A brief analysis of charge rearrangement and is used to rationalize the calculated chemical shifts.

The $\delta_\perp$ and $\delta_\parallel$ components of the isotropic chemical shift were also studied. We corroborate that for the proton hydrogen bonded, the $\delta_\parallel$(H) component is more shielded than the $\delta_\perp$(H). For the proton acceptor O atom, the reverse occurs. The $\delta_\parallel$(O) is less shielded than the $\delta_\perp$(O). These components allow us to evaluate the directional character of each hydrogen bond. We observed that the anisotropic shielding of the O atom in proton acceptor water is lower than in the proton acceptor methanol, showing an isotropy of the hydrogen bond that is larger for the $CH_3OH \cdots OH_2$ than $CH_3HO \cdots H_2O$.

Finally, we considered the effects of monomer relaxation in the calculated NMR parameters. We verified that this effect was appreciable only for the O atom of the OH part of the donor molecule because of the deformation of the O—H distance upon the binding formation.

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References

1. Frank, H. S.; Evans, M. W. J Chem Phys 1945, 13, 507.
2. Soper, A. K.; Finney, J. L. Phys Rev Lett 1993, 71, 4346.
3. D'Angelo, M.; Onori, G.; Santucci, A. J Chem Phys 1994, 100, 3107.
4. Egashira, K.; Nishi, N. J Phys Chem B 1998, 102, 4054.
5. Murthy, S. S. N. J Phys Chem A 1999, 103, 7927.
6. Dixit, S.; Poon, W. C. K.; Crain, J. J Phys Condens Matter 2000, 102, L323.
7. Bowron, D. T.; Soper, A. K.; Finney, J. L. J Chem Phys 2001, 114, 6203.
8. Dixit, S.; Crain, J.; Poon, W. C. K.; Finney, J. L.; Soper, A. K. Nature 2002, 416, 829.
9. Guo, J-H.; Luo, Y.; Augustsson, A.; Kashtanov, S.; Rubensson, J-E.; Shuh, D. K.; Ågren, H.; Nordgren, J. Phys Rev Lett 2003, 91, 157401.
10. Ferrario, M.; Haughney, M.; McDonald, I. R.; Klein, M. L. J Chem Phys 1990, 93, 5156.
11. Tanaka, H.; Gubbins, K. E. J Chem Phys 1992, 97, 2626.
12. Laaksonen, A.; Kusalik, P. G.; Svishchev, I. M. J Phys Chem A 1997, 101, 5910.
13. Fileti, E. E.; Rivelino, R.; Canuto, S. J Phys B 2003, 36, 399.
14. González, L.; Mó, O.; Yanes, M. J Chem Phys 1998, 109, 139.
15. Stockman, P. A.; Blake, G. A.; Lovas, F. J.; Suenran, R. D. J Chem Phys 1997, 107, 3782.
16. Fileti, E. E.; Canuto, S. Adv Quantum Chem 2004, 47, 51.
17. Ludwig, R. Chem Phys Lett 1995, 195, 329.
18. Huelsekopf, M.; Ludwig, R. J Mol Liq 2000, 85, 105.
19. Arnold, J. T.; Packard, M. E. J Chem Phys 1951, 19, 1608.
20. Schneider, W. G.; Bernstein, W. G.; Pople, J. A. J Chem Phys 1958, 28, 601.
21. Becker, E. D.; Liddel, U.; Schoolery, J. N. J Mol Spectrosc 1959, 2, 1.
22. Huggins, C. M.; Pimentel, G. C.; Schoolery, J. N. J Phys Chem 1956, 60, 1311.
23. Asakawa, N.; Kuroki, S.; Kurosu, H.; Ando, I.; Shoji, A.; Ozaki, T. J Am Chem Soc 1992, 114, 3261.
24. Perrin, C. L.; Dwyer, T. J.; Rebek, J.; Duff, R. J. J Am Chem Soc 1990, 112, 3122.
25. Zhou, N. E.; Zhu, B. Y.; Sykes, B. D.; Hodges, R. S. J Am Chem Soc 1992, 114, 4320.

26. Ditchfield, R. Mol Phys 1974, 27, 789.
27. Ditchfield, R. J Chem Phys 1976, 65, 3123.
28. Ditchfield, R. Chem Phys Lett 1976, 40, 53.
29. Rohlfing, C. M.; Allen, L. C.; Ditchfield, R. J Chem Phys 1983, 79, 4958.
30. Rohlfing, C. M.; Allen, L. C.; Ditchfield, R. Chem Phys Lett 1982, 86, 380.
31. Hinton, J. F.; Wolinski, K. In Ab Initio GIAO Magnetic Shielding Tensor for Hydrogen Bonded Systems; Hadži, D., Ed.; Theoretical Treatments of Hydrogen Bonding; John Wiley & Sons, 1997.
32. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. Ab Initio Molecular Orbital Theory; John Wiley & Sons, 1986.
33. Wolinski, K.; Hinton, J. F.; Pulay, P. J Am Chem Soc 1990, 112, 8251.
34. Gauss, J. Chem Phys Lett 1992, 191, 614.
35. Gauss, J. J Chem Phys 1993, 99, 3629.
36. Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. J Chem Phys 1996, 104, 5497.
37. Rauhut, G.; Puyear, S.; Wolinski, J. F.; Pulay, P. J Phys Chem 1996, 100, 6310.
38. Schreckenbach, G.; Ziegler, T. J Phys Chem 1995, 99, 606.
39. Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. J Chem Phys 1996, 104, 5497.
40. Wolinski, K.; Hinton, J. F.; Pulay, P. J Am Chem Soc 1990, 112, 8251.
41. Boys, S. F.; Bernardi, F. Mol Phys 1970, 19, 553.
42. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98W, Revision A.7; Gaussian: Pittsburgh, PA, 1998.
43. Kirschner, K. N.; Woods, R. J. J Phys Chem A 2001, 105, 4150.
44. Chesnut, D. B.; Phung, C. G. Chem Phys 1990, 147, 91.
45. Chesnut, D. B. Ann Rep NMR Spectrosc 1994, 29, 71.
46. Gauss, J.; Stanton, J. F. Adv Chem Phys 2002, 123, 355.
47. Haeberlen, U. High Resolution NMR in Solids; Academic Press: San Diego, CA, 1976.
48. Tesche, B.; Haeberlen, U. J Magn Reson A 1995, 117, 186.
49. Gauss, J. Chem Phys Lett 1994, 229, 175.
50. Gauss, J.; Stanton, J. F. J Chem Phys 1995, 103, 3561.
51. Karadakov, P. B. J Mol Struct 2002, 602, 293.
52. Fowler, P. W.; Raynes, W. T. Mol Phys 1981, 43, 65.
53. Fukui, H.; Baba, T.; Narumi, J.; Inomata, H.; Miura, K.; Matsuda, H. J Chem Phys 1996, 105, 4692.
54. Pecul, M.; Leszczynski, J.; Sadlej, J. J Chem Phys 2000, 112, 7930.
55. Kitzinger, J. P. NMR Basic Principles Prog 1982, 17, 1.
56. Jameson, C. J.; Jameson, A. K.; Oppusunggu, D.; Wille, S.; Burrell, P. M.; Mason, J. J Chem Phys 1981, 74, 81.
57. Chauvel, J. P.; True, N. S. Chem Phys 1985, 95, 435.
58. Wasylishen, R. E.; Mooibroek, S.; Macdonald, J. B. J Chem Phys 1971, 75, 932.
59. Wasylishen, R. E.; Bryce, D. L. J Chem Phys 2002, 117, 10061.
60. Hindman, J. C. J Chem Phys 1966, 44, 4582.
61. Vaara, J.; Lounilla, J.; Ruud, K.; Helgaker, T. J Chem Phys 1998, 109, 8388.
62. Tostes, J. G. R.; Dias, J. F.; Seidl, P. R.; Carneiro, J. W. M.; Taft, C. J Mol Struct (Theochem) 2002, 580, 75.