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Ab Initio Quantum Mechanical Calculation of the Chemical Shift Anisotropy of the Hydrogen Atom in the $(H_2O)_{17}$ Cluster

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Abstract: The chemical shift anisotropy ($\Delta\sigma$) of the hydrogen atom in the $(H_2O)_{17}$ cluster has been calculated using the gauge-independent atomic orbital method (GIAO). The value obtained of $\Delta\sigma$ = 34.83 ppm is in agreement with the experimental value determined for ice obtained by two independent studies. The calculated chemical shift results presented illustrate the use of an efficient procedure that permits one to perform theoretical chemical shift calculations on relatively large molecular systems.

Introduction

Recently, a procedure was published[1] for the use of the gauge-independent atomic orbital (GIAO) method[2] for the calculation of NMR chemical shifts. The results of this procedure were compared to those obtained by localized methods[3,4] and the advantages of the GIAO method discussed. As part of a program to test the new GIAO procedure, we wish to report the results of the calculation of the chemical shift anisotropy for the hydrogen atom in the $(H_2O)_{17}$ cluster. This system was chosen for study for a number of reasons: (1) It contains a relatively large number of heavy atoms, 17. Using large basis sets for the calculation, the program efficiency is, therefore, tested. (2) Experimental NMR measurements have been made on ice to determine the chemical shift anisotropy of the hydrogen atom.[5-8] Significantly different values of the chemical shift anisotropy were obtained. Previous calculations, using a small basis set, for the $(H_2O)_5$ cluster did not adequately resolve the issue.[9] Consequently, it was of interest to determine if the new method, as applied to a larger cluster, would serve to indicate which values are better. (3) The experimental values were obtained at very low temperatures, 173–195 K. Consequently, influences of vibrational and librational effects on the chemical shift anisotropy are minimized in the comparison with the calculated value which represents the $(H_2O)_{17}$ cluster at 0 K. (4) The crystal structure of ice has been determined at 123 K.[10] Therefore, theoretical geometry optimization was not necessary for obtaining the cluster structure required for the chemical shift calculation. (5) Finally, the effect of a second sphere of solvent molecules on the chemical shift anisotropy can be ascertained from comparison of the value for the central water molecule in the $(H_2O)_5$ and $(H_2O)_{17}$ clusters.

Table I. Principal Components of the Chemical Shift Tensor (σ) and Chemical Shift Anisotropy [$\Delta\sigma = \sigma_{zz} - (\sigma_{xx} + \sigma_{yy})/2$]

water	σ_{xx} (ppm)	σ_{yy} (ppm)	σ_{zz} (ppm)	$\Delta\sigma$ (ppm)
$(H_2O)_1$[a]	24.77	26.54	41.36	15.71
$(H_2O)_2$[a]	18.60	19.57	46.07	26.99
$(H_2O)_3$[a]	17.21	18.36	48.70	30.92
$(H_2O)_5$[a]	15.77	16.27	48.19	32.17
$(H_2O)_5$[b]	12.35	13.43	47.13	34.24
$(H_2O)_5$[c]	12.30	13.32	47.72	33.92
$(H_2O)_{17}$[b]	11.98	12.25	47.28	35.17
$(H_2O)_{17}$[d]	11.97	12.19	46.91	34.83
ice[e,i]	−6.5	−6.5	27.7	34.2 ± 1
ice[f,i]	−19	−19	15	34 ± 4
ice[g,i]	−12.5	−12.5	16	28.5 ± 1
ice[h,i]	−17.5	−17.5	11.2	28.7 ± 1

[a] Reference 9. Calculations performed with a 4-31G basis set on all atoms. The values listed are those for the chemical shielding not chemical shift with respect to a reference. [b] In the present work, a 6-311G+1p+1d basis set was used for the central O–H···O atoms and 4-31G on all others. The values listed are those for the chemical shielding not chemical shift with respect to a reference. [c] In the present work, a 6-311G+1p+1d basis set was used for all atoms. [d] In the present work, a 6-311G+1p+1d basis set was used for all atoms in the central water molecule and those in the four water molecules in first hydration sphere, and a 4-31G basis set was used for the twelve water molecules in the second hydration sphere. The values listed are those of the chemical shielding and not chemical shift with respect to a reference. [e] Reference 5. Temperature was 173 K. [f] Reference 6. Temperature was 183 K. [g] Reference 7. Temperature was 195 K. [h] Reference 8. Temperature was 195 K. [i] Liquid water was used as a chemical shift reference.

Results and Discussion

Table I contains the calculated and experimental values of the principal components of the chemical shift tensor and the chemical shift anisotropy for water clusters at 0 K and ice. The new calculated results presented in this paper were obtained with an IBM RS/6000 computer. Several basis sets and basis set combinations were used to determine the overall size necessary to obtain accurate chemical shift parameters. When calculations are performed on relatively large molecular systems containing many heavy atoms, the optimum basis set or basis set combination to be used is of critical importance because of the accompanying computer demands. For the $(H_2O)_5$ cluster, chemical shift calculations were performed with two basis sets and a basis set combination; 4-31G basis set on all atoms, 6-311G+1p+1d basis set[11] on all atoms, and an "attenuated" basis set in which the 6-311G+1p+1d basis set was used for the central O–H···O atoms and the 4-31G basis set was used for all of the other atoms. The "attenuated" basis set procedure has been suggested by Chesnut.[12,13] Previous results have shown that the 6-311G(d,p) basis set is near the Hartree–Fock limit for the first-row elements.[12] The data contained in Table I reveal the necessity of using a large basis set to, at the least, describe the central hydrogen-bonded atoms, O–H···O. A difference of about 2 ppm results if only a 4-31G basis set is used for all of the atoms in the $(H_2O)_5$ cluster. However, the "attenuated" basis set gives essentially the same

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result as the 6-311G+1p+1d basis set on all of the atoms but takes half the computer time. It should be noted that the data in Table I compare the calculated absolute shieldings with experimental chemical shifts, and thus, a constant difference is expected between the two sets of results. This, however, does not affect the chemical shift anisotropy.

For the $(H_2O)_{17}$ cluster, calculations were performed employing two basis set combinations. With one calculation, the 6-311G+1p+1d basis set was used for the central O–H···O atoms involved in the hydrogen bond and a 4-31G basis set was used for all other atoms. A second calculation was performed with the $(H_2O)_{17}$ cluster in which the central water molecule and the four first-sphere hydration water molecules were described by the 6-311G+1p+1d basis set while the remaining twelve second-sphere hydration water molecules were described by the 4-31G basis set. The calculated values of the chemical shift anisotropy (35.17, 34.83 ppm) for the central water hydrogen atom involved in a hydrogen bond in the $(H_2O)_{17}$ cluster are in very good agreement with those values of about 34 ppm obtained experimentally[5,6] but are quite different from the experimentally determined value of about 28.6 ppm.[7,8] Electron correlation effects for a molecular system such as the water cluster would be unlikely to make a significant contribution to the shielding. Therefore, the calculations presented in this paper support the higher values obtained experimentally but, of course, cannot provide an explanation for the discrepancy between the two sets of experimental values. The two basis set combinations used for these calculations gave essentially the same results; however, the time required for the two calculations was significantly different. The calculation for the system in which the five water molecules were described by the 6-311G+1p+1d basis set and the second-sphere water molecules described by the 4-31G basis set required 14 h as opposed to 8 h for the system in which only the central hydrogen bond atoms were described by the 6-311G+1p+1d basis set. The loss in accuracy is minimal while the time saved with the smaller basis set combination is signficant.

The calculated isotropic chemical shift $[(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3]$ for the central hydrogen atom is about 7.6 ppm with respect to TMS. This value was obtained by first determining the chemical shift with respect to CH_4 (calculated isotropic shielding value is 31.67 ppm) and correcting for the chemical shift difference between CH_4 and TMS (−0.24 ppm). The experimentally determined chemical shift of liquid water at 298 K with respect to TMS is about 4.8 ppm. Therefore, the chemical shift of the hydrogen in the ice cluster at 0 K is 2.9 ppm downfield from liquid water at 298 K. The magnitude of this chemical shift appears to be quite reasonable in view of the fact that there is a downfield shift of 0.4 ppm in liquid water over the temperature range of 298 K to the supercooled state of liquid water at 258 K.[14] Unfortunately, a comparison of the calculated value of the isotropic chemical shift with experimental values is difficult. Perusal of the experimental data in Table I shows that there is considerable disagreement between the principal component values and the isotropic chemical shift. These differences have been commented upon; however, the authors were unable to explain them.[3,5] Obviously, the best comparison of calculated and experimental chemical shift parameters relies upon that of the chemical shift anisotropy since this comparison does not involve the experimental problems of referencing, bulk susceptibility corrections, and magnetic field strength stabilization.

The need to include a second sphere of water molecules in the calculation can be seen from a comparison of the calculated value of the chemical shift anisotropy of the central hydrogen atom in the $(H_2O)_5$ and $(H_2O)_{17}$ clusters. The addition of the second sphere of water molecules increases the chemical shift anisotropy by 0.98 ppm. This result illustrates the potential importance of considering long-range solvent effects in chemical shift calculations. The chemical shift anisotropy more than doubles upon completing the first solvation sphere and increases by about 1 ppm with the addition of the second solvation sphere. Further addition of a third sphere would probably have very little effect on the chemical shift parameters. It should also be noted that the σ_{xx} and σ_{yy} tensor components become almost identical in the $(H_2O)_{17}$ cluster, being only different by 0.27 ppm. This is in agreement with the prediction of approximate axial symmetry for the shielding associated with O–H···O hydrogen bonds.[15] Such a small difference in principal component values would be difficult to observe experimentally and probably explains why the powder pattern of ice appears to be axially symmetric in the experimental spectra. For the $(H_2O)_5$ cluster these tensor components differ by 1.08 ppm. Again, the need to account for long-range solvent effects is evident.

In summary, the GIAO method, with a sufficiently large basis set or basis set combination, can provide accurate chemical shift parameters for relatively large molecular systems containing many heavy atoms in an efficient manner. The results obtained for the $(H_2O)_{17}$ cluster show the practical application of such calculations to the problem of discerning which of two sets of experimental data is the more accurate. The importance of the inclusion of secondary hydrogen bonding on the chemical shift parameters is also illustrated and must be considered if one suspects solvent effects, such as hydrogen bonding, to be present.

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