MAGNETIC SHIELDING PROPERTIES OF WATER IN VARIOUS MOLECULAR AND MOLECULAR-IONIC STRUCTURES

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Dedicated to Prof. Dr. Dr. h. c. Hartmut Fuess (Darmstadt Technical University, Germany)
on the occasion of his 65th birthday

[1]H and [17]O magnetic shielding tensors of water molecules in various water clusters, as well as in water–pyridine H-bond complexes and in molecular-ionic structure of $Br^-(H_2O)_6$ have been calculated using density functional theory. The full geometry optimization was performed in the framework of Becke's three parameter hybrid method and the Lee–Yang–Parr correlation functional (B3LYP) combined with 6-311++G** basis set. Magnetic shielding tensors have been calculated using the hybrid functional of Perdew, Burke, and Ernzerhof (PBE1PBE) and the gauge-including atomic orbital (GIAO) approach was applied to ensure gauge invariance of the results. Solvent effects were taken into account by polarizable continuum model (PCM). The calculated NMR parameters are compared with the corresponding experimental data for aqueous system, which exhibit an unusual critical behaviour and phase transitions.

Keywords: density functional theory, properties of molecules and molecular ions, line and band widths, shapes and shifts, NMR and relaxation

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1. Introduction

A boosted interest in magnetic screening properties of water molecules is caused by several reasons. First of all, a growing flux of works on magnetic resonance imaging (MRI) and its applications in medicine, biology, ecology, and other fields has to be mentioned [1–3]. Water molecules play a crucial role in many processes there. Furthermore, dissolving certain organic solute / ionic subsystems in water, peculiar aqueous solutions may be composed. They exhibit many strange, sometimes even paradoxical features of fundamental importance. Several extremely challenging problems are met there: hydrophobic and structure effects [4, 5], non-equilibrium restructuring, criticality and crossover between the solvophobic and ionic regimes [6–8], supercritical state of water [9]. This made the water systems as a certain 'firing ground' for many experimental works, NMR among them, and for many developments in theory of condensed matter statistical physics and quantum chemical calculations. Studies of mentioned problems by NMR spectroscopy, beside the data from statistical physics and thermodynamics, require the knowledge of certain *micro*-parameters, *viz* magnetic shielding tensors of various water aggregates. Because of fast molecular motion the NMR signal shifts in the liquids are determined by isotropic part of magnetic shielding tensors of corresponding nuclei. Most significant last period works on magnetic shielding properties of water are devoted either to pure quantum chemistry calculations or to some joint treatments applying molecular dynamics and chemical equilibrium theories [10–19]. Unfortunately most of them deal with water structures *in vacuo*, or presented data sets are not complete enough for the modelling of NMR spectra of mentioned systems.

The purpose of the present work was to investigate ^{1}H and [17]O magnetic shielding tensors of water molecules in various water clusters, also in water–pyridine H-bond complexes and in ionic structure of $Br^-(H_2O)_6$ by means of density functional theory (DFT) calculations taking into account solvent effects by polarizable continuum model (PCM).

2. Method of calculations

Magnetic shielding tensor calculations of water molecules in considered clusters have been performed using DFT. The applied approach was checked in various cases earlier [20, 21] and found to be adequate for this purpose. It produces an excellent agreement between calculated and experimentally measured ^{1}H NMR shift for nuclei in very strong H-bond systems, e. g. bridge proton in pyridine-N-oxide...HCl complex [20], as well as for rather "inert" groups, e. g. –CH$_3$ protons of acetonitrile [21].

In more detail, the full geometry optimization in the ground state was performed in the framework of Becke's three parameter hybrid method and the Lee–Yang–Parr correlation functional (B3LYP) combined with 6-311++G** basis set [22–24]. Gaussian 03, Revision B.05 package [25] was used for all calculations. Magnetic shielding tensor $\boldsymbol{\sigma}^X$ of a nucleus X is expressed as a second derivative of the free energy G with respect to the external magnetic field $\boldsymbol{B}$ and the nuclear magnetic moment $\boldsymbol{\mu}^X$,

$$\sigma_{ij}^X = \frac{\partial^2 G}{\partial B_i\,\partial \mu_i^X}\,, \qquad (1)$$

where $i, j = x, y, z$ denote corresponding Cartesian components. These tensors have been calculated using the 1997 hybrid functional of Perdew, Burke, and Ernzerhof (PBE1PBE) [26, 27], and the gauge-including atomic orbital (GIAO) approach [28] was used to ensure gauge invariance of the results. In order to take solvent effects into account we have applied the polarizable continuum model [29, 30]. In this approach the free energy G is defined as a functional of the solute electronic wave function Ψ,

$$G(\Psi) = \langle\Psi|\boldsymbol{H}^0|\Psi\rangle + \langle\Psi|\frac{1}{2}\boldsymbol{V}^R|\Psi\rangle\,, \qquad (2)$$

where $\boldsymbol{H}^0$ is the Hamiltonian describing the isolated molecule and $\boldsymbol{V}^R$ represents the solvent reaction field operator. In the PCM the reaction potential includes only electrostatic solvent–solute interactions. Other contributions, i. e. steric, dispersive, and repulsive interactions, are calculated by classical algorithms, modifying the solute energy but not its wave function. This model is implemented in Gaussian 03 program package in a user friendly way [25].

The ^{1}H chemical shifts of the investigated molecular structures (water clusters and pyridine / water H-bond complexes) were transformed to the δ-scale as the difference between the calculated isotropic magnetic
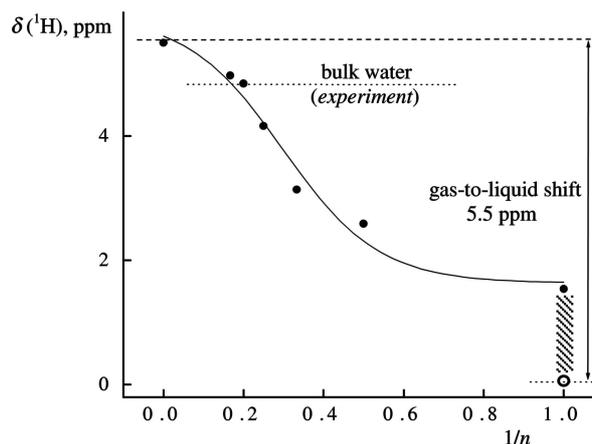

Fig. 1. ^{1}H NMR shift of structures (H$_2$O)$_n$ at increasing number of aggregation n calculated including reaction field of water. Presentation in $1/n$ as variable was chosen for convenience to put the limiting case $n \to \infty$ to the graph. Experimental values of water monomer in various solvents (taken from [37]) are shown by dashed area. Calculated monomer shift *in vacuo* is shown by open circle, pentamer and hexamer shifts are taken from [16]. More comments in text.
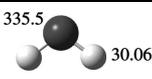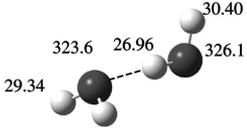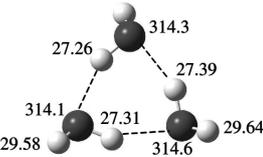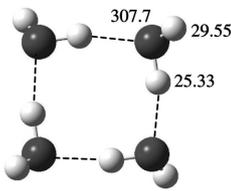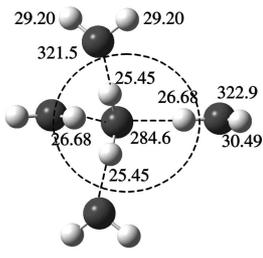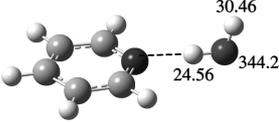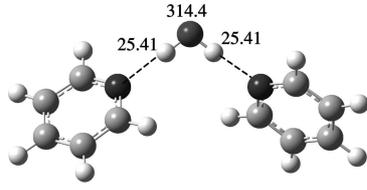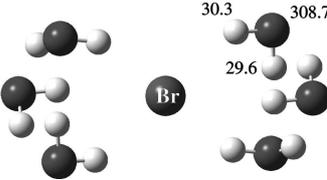
shielding (σ_{iso}) and that of the tetramethylsilane (TMS) as a reference molecule [20, 31].

3. Results and discussion

Several water structures, closely related to peculiar restructuring effects close in the vicinity of the phase transition [5, 6], have been chosen, and their magnetic screening properties have been studied. All calculated molecular aggregates, values of isotropic part of magnetic screening tensors of ^{1}H and ^{17}O nuclei, as well as their chemical shifts $\langle\delta\rangle$, where $\langle\ldots\rangle$ denotes an averaging over all "mobile" (i. e. enrolled into fast exchange processes) protons in corresponding structure are collected in Table 1. The latter quantity is measured in most liquid-state NMR experiments. For more convenient discussion and comparison with experimental data some calculated parameters are presented in Figs. 1 and 2.

A certain experimental support for existence of optimized water structures, i. e. near-linear hydrogen bonded dimer, cyclic trimer, and cyclic tetramer (Table 1), comes from measurements of vibration–rotation tunnelling and low temperature matrix isolation FTIR spectra of water [32–35]. It is obvious that a segregation of pure dimer, trimer, etc. in the liquid water is not realizable; therefore NMR shifts of these structures have never been evaluated experimentally because of dynamic averaging. Consequently, a comparison of calculated NMR shifts and experimental data is

Table 1. Calculated structures, isotropic parts of ^1H and ^{17}O magnetic screening tensors and ^1H NMR chemical shift $\langle\delta\rangle$ averaged over all protons in structure (all in ppm). Chemical shifts were recalculated with respect to TMS molecules as NMR standard using $\sigma_{iso}(^1H, TMS) = 31.6$ ppm (in water).

No.	Structure	Screening	Chemical shift $\langle\delta\rangle$
I	Non-bonded water (monomer, C_{2v} symmetry)	335.5 30.06	1.54
II	Dimer (C_s)	30.40 323.6 26.96 326.1 29.34	2.59
III	Trimer (C_1)	314.3 27.26 27.39 314.1 27.31 29.64 29.58 314.6	3.14
IV	Tetramer (S_4)	307.7 29.55 25.33	4.16
V	Pentamer (T_dC_{2v}) [a]	29.20 29.20 321.5 25.45 322.9 26.68 26.68 284.6 30.49 25.45	5.5
VI	Water–pyridine 1 : 1 complex (C_s)	30.46 24.56 344.2	4.25
VII	Water – pyridine 1 : 2 complex. (C_1)	314.4 25.41 25.41	6.19
VIII	$Br^-(6H_2O)$ structure (S_6) [b]	30.3 308.7 29.6 Br	1.65

[a] T_d tetrahedral symmetry for oxygen was frozen and 'qudratically convergent SCF' procedure was used;

[b] geometry optimization and magnetic shielding calculation performed at B3LYP / aug-cc-pVDZ and B3PW91 / 6-311G** level of theory respectively.
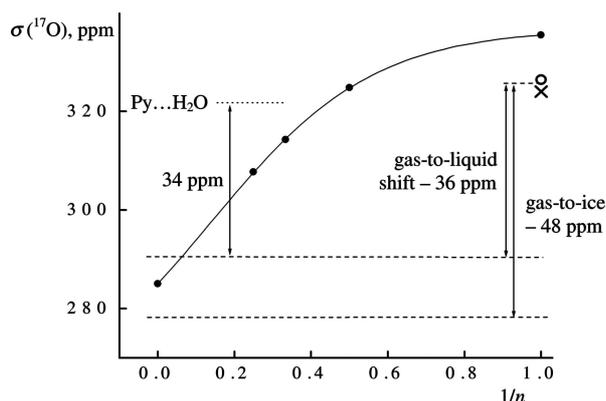
Fig. 2. ^{17}O isotropic magnetic screenings of $(H_2O)_n$ and Py–H_2O complex calculated including reaction field of water. Monomer screenings *in vacuo* (∘ – present work, × – taken from recent high-level calculations [14]) are presented in order to illustrate gas-to-liquid and gas-to-ice shifts [11].

possible for the bulk and "monomeric" water only. Experimental data are well-known: 4.72 ppm in the bulk water [36], whereas at an infinite dilution in various solvents the chemical shift values are spread over 0.4–1.4 ppm depending on the solvent [37]. This region is shown as a dashed area in Fig. 1. The calculation of "monomeric" water gives the values of its chemical shift about 0.1 ppm *in vacuo* and 1.54 ppm in water as a solvent. It is hard to expect a better agreement with the experimental values (e. g. 0.4 ppm in benzene, 1.2 ppm in CCl_4, 1.4 ppm in $C-6H_{12}$ [37]) since no additional corrections due to different solvents magnetic susceptibility effects or rovibrational averaging were made.

^1H NMR shifts of $(H_2O)_n$ increase with increasing aggregation number n, and already in pentamer and hexamer they top a bulk water value (Fig. 1). Therefore, these structures are considered as dominant ones in the liquid water [16]. In addition a tetrahedrally-coordinated pentamer (Structure *V*, Table 1) was studied in the present work in order to evaluate the chemical shift of water in the limiting aggregation case of $n \to \infty$. This structure was optimized keeping tetrahedral symmetry for oxygen atoms frozen and including reaction field of water via PCM. The ^1H NMR shift of 5.5 ppm was obtained by averaging the chemical shifts of "internal" protons (circled protons in *V*, Table 1). The obtained $\delta(^1H)$ value, being in agreement with a gas-to-liquid shifts of 5.8±0.1 ppm [11], limits the whole extent of chemical shifts of water in the liquid state. It lies between those of bulk water (4.72 ppm) and ice (∼8 ppm [11]). The NMR shift in ice has not been reached even when only two "central" protons of tetrahedral pentamer are averaged (6.2 ppm). It may be due to the fact that PCM model does not describe an

ordered crystalline field satisfactory, or this pentamer is still too small for major short-range interactions in ice to be taken into account.

The last three structures (*VI–VIII*, Table 1) are particularly important studying non-equilibrium restructuring, criticality, and crossover mentioned above [5–7]. Namely, a broad variety of phase transitions are known in aqueous solutions of different pyridine derivatives. Binary systems of water / pyridine and water / one-methyl-substituted pyridine are completely miscible, however the systems of water / two-methyl-substituted pyridine and water / one-ethyl-substituted pyridine exhibit very fascinating closed-loop phase diagrams [38]. Phase separation in completely miscible water / pyridine mixtures can be induced by introduction of ionic subsystem [5, 6]. A very strong effect of ions on NMR shifts was observed in [5] for water / 3-methylpyridine(3MP) / NaBr solutions, and much stronger action of anions, i. e. Br^- (that are well-known structure breakers), than cations (Na^+) was stressed. By dissolving of NaBr up to 0.2 mass fractions in binary water / 3MP mixture the water ^1H NMR signal shifts from about 5 to 4.5 ppm. The further increase in concentration of salt leads to the appearance of two immiscible phases and to the signal doubling. It is somewhat rather strange result because due to very strong H-bond between water and pyridine molecules much larger values of NMR shift are expected, e. g. up to ∼6 ppm, as in water...pyridine 1 : 2 complex (*VII*, Table 1). Comparing magnetic screening data for *VI–VIII* structures it is easy to see that even a very small amount of Br^- ions can cause large decrease (up to 1.65 ppm!) in chemical shift of six water molecules placed in the first hydration shell of ion. Hence, an increase of chemical shift due to the strong water...pyridine H-bond is compensated by large decrease due to the water-ionic interactions.

In case of ^{17}O nuclei a comparison of the theoretical data with the experiment data is more complicated. In many cases the $D_2{}^{17}O$, which usually is used for lock, is also used as the reference for the ^{17}O NMR spectra. A calculation of the reference screening, i. e. liquid water, is therefore complicated. For this reason instead of chemical shifts, absolute values of ^{17}O magnetic shielding are presented in Fig. 2. Recently the value of 324.0±1.5 ppm has been proposed as a reference for ^{17}O absolute shielding scale in the gas phase [14]. After some additional snapshots from molecular dynamics simulation and crystal data for ice were taken into account the so-called gas-to-liquid and gas-to-ice shifts have been determined [11]. They are shown in

Fig. 2. The ^{17}O magnetic screening of water monomer *in vacuo* (326.4 ppm) calculated in this work is in a perfect agreement with the above given value for gas phase obtained from high-level calculations including rovibrational effects [14]. The solvent (water) reaction field shifts this value up to 335.5 ppm. Hence, the changes in ^{17}O NMR signal positions of water structures are spread between the values of monomer in water solvent and ice. Note that, as in the case of ^1H NMR shifts, the ^{17}O magnetic shielding value of the "central" oxygen in tetrahedral pentamer lies again between those of bulk water and ice (Fig. 2). Also note a surprisingly large calculated ($\sim+34$ ppm) ^{17}O NMR shift within pyridine...H_2O complex with respect to bulk water, whereas a corresponding experimental value is about +8 ppm only [39]. This discrepancy is extremely important. It supports an idea that in real aqueous solutions a partial pyridine protonation (Py H^+) and appearance of OH^- may occur. The chemical shift of OH^- is about -70 ppm [39], and thereby even a small amount of these ions can cause the experimentally observed reduction in chemical shift up to 8 ppm. However the protonation of pyridine in aqueous solution is probably a rather collective phenomenon, which covers the action of many water molecules, and therefore huge water clusters have to be included in the calculation [40]. This problem can stimulate new developments in modelling of molecular systems.

4. Concluding remarks and outlook

Despite rather simple theoretical model applied in this work (a standard PBE1PBE functional together with PCM), a nice agreement between obtained numbers and corresponding experimental data was found. Our results compare with high-level calculations (coupled clusters, MP2) fairly well. It serves as an extra support to one type of calculations that is widely used and leads to good results. Namely, the short-range interactions, usually presented in condensed phases, can be effectively handled by 'supermolecule' calculations (i. e. the model of a solute molecule surrounded by several solvent molecules (in our case – water)) and an inclusion of solvent reaction field provides an effective description of long-range electrostatic interactions [41]. Only in the case of ice this concept may work not satisfactorily, or a larger 'supermolecular' aggregate has to be built.

Finally, an excellent agreement between PBE1PBE + PCM calculation results and experimental data has to be noted not only for ^1H NMR of water and water-ionic solutions, but also for ^{13}C and ^{17}O magnetic screenings in many other molecular systems, and particularly, in studying hydrogen bonding and proton transfer processes [42]. Obtained data on magnetic screening properties of water structures will also be used to explain temperature dependences of ^1H and ^{17}O NMR shifts and to model critical behaviour of chemical shift close to the phase separation point.

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MOLEKULINIŲ VANDENS BEI VANDENS IR JONŲ DARINIŲ MAGNETINIO EKRANAVIMO SAVYBĖS

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Santrauka

Pastarųjų metų tyrimai kelia vis didėjantį susidomėjimą įvairių vandens darinių (tirpalų, elektrolitinių sistemų) savybėmis ir parametrais. Vanduo yra svarbiausia medžiaga gyvojoje gamtoje, todėl sparčiai auga skaičius darbų, kuriuose taikomi šiuolaikiniai branduolinio magnetinio rezonanso (BMR) tomografijos metodai. Be to, dariniuose vanduo / organinis sandas / joninė posistemė dažnai aptinkami struktūriniai bei faziniai virsmai, kurie labai skatina statistikinės kondensuotųjų terpių fizikos pažangą. Šiame darbe pateikiami įvairių vandens molekulinių ($(H_2O)_n$ spiečiai ($n = 1 \ldots 5$), H_2O vandenilinio ryšio kompleksai su piridinu) bei vandens ir jonų ($Br^- (H_2O)_6$) darinių ^1H ir ^{17}O branduolių magnetinio ekranavimo tenzorių skaičiavimo rezultatai kvantinės chemijos *ab initio* tankio matricos metodu 6-311G** bazėje visiškai optimizuojant tiriamųjų molekulių geometriją. Optimizavimui buvo panaudotas Becke hibridinis trijų parametrų metodas kartu su Lee, Yang ir Parr'o funkcionalu (B3LYP). Skaičiuota 6-311++G** funkcijų bazėje. Magnetinio ekranavimo tenzoriams skaičiuoti buvo pritaikytas hibridinis Perdew, Burke ir Ernzerhof'o funkcionalas (PBE1PBE) ir GIAO atominės orbitalės. Į tirpiklio reakcijos lauką buvo atsižvelgta, pritaikius poliarizuotojo kontinuumo modelį (PCM-IEF). Taip apskaičiuoti vandens ^1H ir ^{17}O branduolių ekranavimo parametrai gerai dera su atitinkamais eksperimentiniais BMR spektrometrijos duomenimis. Rezultatai bus pritaikyti tolesniuose tyrimuose, aiškinant vandens BMR signalų temperatūrines priklausomybes bei restruktūrizavimosi reiškinius kriziniuose vandens tirpaluose.