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Nuclear Magnetic Resonance Parameters of Water Hexamers

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Nuclear magnetic resonance ^1H , ^{16}O , and ^{17}O chemical shifts, as well as ^{17}O quadrupolar parameters in several isomers of water hexamer clusters, are studied using density functional theory calculations and the gauge including projector augmented wave (GIPAW) pseudopotential method. The prism, cage, book, bag, chain, and two cyclic isomers are investigated, and structures with ^{16}O and ^{17}O nuclei are examined. It is found that the hydrogen and oxygen chemical shifts show a substantial variation. In six more stable hexamers, all quadrupole coupling constants decrease and asymmetry parameters increase in a comparison with bulk water, whereas a chain isomer shows an opposite behavior. The values of NMR parameters are in reasonable agreement with existing results obtained by more computationally demanding methods.

1. Introduction

Water clusters are the subject of intensive research because of many unusual properties of this important material.^{1–9} It is known that water shows many unusual properties.^{10–13} For example, the volume, the diffusion coefficient, the heat capacity, the compressibility, and the viscosity of water depend non-monotonically on temperature or pressure. The water volume contracts on melting, and its solid phase exists in at least 15 crystalline and several amorphous modifications. Liquid water is essential for life on Earth, but light and heavy water show different activity in biological systems. The complex behavior of water is apparent already at nanoscales. Theoretical studies of bulk water have shown that this material is often better described as a collection of clusters than as an isotropic medium.¹² Hexamers are at the border between the smallest clusters, where cyclic planar structures prevail, and bigger three-dimensional morphologies with motifs of bulk liquid water and ice. Several isomers of a water hexamer are known.^{1–8} Their energies are distributed in a small interval, but, although almost isoenergetic, these isomers exhibit a different point group symmetry and different numbers of hydrogen bonds and donor–acceptor monomers. Consequently, water hexamers differ in other properties, for example in dipole moments and the O–H vibrational spectra.^{1–8}

Nuclear magnetic resonance (NMR) is a powerful technique used in physics, chemistry, biology, and medicine. In all these fields water is of the greatest importance. NMR measurements are sensitive to the local electronic structure of materials. Therefore, this technique is a useful tool for studies of O and H nuclei in pure water and aqueous solutions. Water is often visible in ^{17}O NMR spectra of biomolecules, and analysis of NMR parameters of pure water is also useful in this field.¹⁴ NMR parameters of the hydrogen nuclei in bulk liquid water show involvement of this atom in H-bonding.¹⁵ Hydrogen bonding interactions depend on the local density and on the orientation of water molecules near a specific hydrogen atom. The hydrogen bonding in liquid water is still not completely understood.^{10,16–18} On the basis of X-ray absorption spectroscopy and X-ray Raman scattering measurements, it has been suggested that most molecules in liquid water exist in two hydrogen-bonded

structures.¹⁶ Such configurations are linear chains and rings of water molecules. Other measurements and calculations suggest that molecules in liquid water exist mainly in hydrogen-bonded tetrahedral configurations.¹⁸

Theoretical studies of NMR parameters give precise properties of the local environment and help to analyze NMR spectra.^{19–21} Traditional quantum chemistry calculations based on the atom-centered basis sets are used in this field, but in applications these methods are biased toward finite systems. The pseudopotential density functional theory (DFT) method is based on periodic boundary conditions. This type of calculation is computationally less intensive than all-electron methods. Pseudopotentials are used in investigations of many properties of nanoparticles, surfaces and bulk of various materials important in physics, chemistry and biology.²² The pseudopotential density functional theory of NMR parameters for extended systems, such as crystals where applications of periodic boundary conditions are necessary, has been introduced.^{23,24} The gauge including projector augmented wave (GIPAW) method has been further developed to study NMR parameters using pseudopotentials to describe not only valence electrons but also those that are close to atomic nuclei.²⁵ This method is computationally efficient and has produced results for NMR parameters of several materials in good agreement with all-electron methods.^{25,26} GIPAW extends the projector augmented wave (PAW) method²⁷ to the cases where the magnetic field is present. In the GIPAW method all-electron response is reconstructed from pseudopotentials. It is possible to use GIPAW for both finite and extended systems of the same material.

Ab initio studies of NMR shielding constants of bulk water under normal and supercritical conditions have been carried out using DFT and configurations generated by the Car–Parrinello molecular dynamics.^{28,29} DFT NMR calculations for the hexagonal ice have also been done.²⁸ Liquid and solid bulk phases of water in quantum chemistry calculations of NMR properties have been modeled using free boundary conditions with a number of molecules similar to hexamers studied here.^{30,31} NMR shielding parameters of several water clusters have been studied using the Gaussian quantum chemistry code.^{32–35} The gauge-including atomic orbitals (GIAO) method has been used, and clusters have been optimized at MP2(FC)/G-311+G(d,p),³² MP1PW91/6-311+G(2d,p),³³ and HF/6-31(d,p) levels.³⁵ Ludwig

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carried out calculations using the B3LYP and Møller–Plesset (MP2) level of theory, as well as 6-31+G* and 6-311++G** basis sets.³⁴ Morphologies of water clusters studied in this work are not necessarily fragments of bulk water or ice. These structures have been confirmed in experiments¹ and other calculations.^{2–8} Hydrogen and oxygen chemical shifts of several water hexamers having ¹⁶O and ¹⁷O nuclei (making together 14 clusters) are calculated using DFT and the GIPAW pseudopotential method. The quadrupole NMR parameters for ¹⁷O nuclei in all its hexamers are studied by using the PAW DFT method that has produced an agreement with experimental results for several materials.^{27,36,37}

2. Computational Methods

In this work chemical shifts and electric field gradients are calculated. Electrons in materials shield an applied external magnetic field \vec{B} and nuclei interact with an effective field $\vec{B}_{\text{in}}(\vec{r})$

$$\vec{B}_{\text{in}}(\vec{r}) = -\hat{\sigma}(\vec{r})\vec{B} \quad (1)$$

In this equation $\hat{\sigma}(\vec{r})$ is the nuclear shielding tensor for a specific nucleus and in a specific chemical environment. Experimental results are often given as the relative chemical shift

$$\delta(\vec{r}) = \sigma^{\text{ref}} - \sigma(\vec{r}) \quad (2)$$

where σ^{ref} is defined for a chosen nucleus in a reference compound and $\sigma(\vec{r}) = (1/3)\text{Tr}[\hat{\sigma}(\vec{r})]$ is the isotropic shielding. Chemical shifts are usually reported in units of 10^{-6} ppm. The electric field gradient (EFG) tensor is a matrix of the second derivatives of the electrical potential V with respect to the spatial coordinates, at the position of the nuclei. EFG tensor describes the asymmetry of the charge distribution that forms as a result of chemical bonding and shows the effect of the surrounding particles on a chosen nucleus in the cluster or bulk. The quadrupolar coupling constant C_Q and the asymmetry parameter η are defined as

$$C_Q = \frac{eQV_{zz}}{h} \quad (3)$$

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (4)$$

where Q is the nuclear quadrupolar momentum, e is the electron charge, h is the Planck constant, and V_{xx} , V_{yy} , and V_{zz} are principal components of the EFG tensor under the following choices: $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. The nuclear quadrupolar momentum of oxygen is $Q = -25.58 \times 10^{-31} \text{ m}^2$.³⁸ However, NMR experiments usually do not provide the sign of the quadrupolar coupling constant.

Calculations are carried out by the GIPAW module of Quantum-ESPRESSO.³⁹ The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) is used.⁴⁰ The norm-conserving GIPAW pseudopotentials prepared by Seitsonen are applied.⁴¹ It has been found that at least two projectors per channel are necessary in the GIPAW method.²⁵ Therefore, the oxygen pseudopotential with two projectors is used. A plane wave energy cutoff of 85 Ry is applied. Water clusters are positioned in the center of the periodically repeated cubic box with the side of 40 au. The most stable hexamers (prism, cage,

book, bag, and two cyclic isomers) are investigated. The initial coordinates of these six isomers optimized and provided by the authors of ref 4 are taken. These isomer forms are most often studied in the recent literature.^{1–7} However, helical water chains have been also investigated.^{8,9} Although less stable than several other isomers, such chainlike structures may exist in porous materials, clathrate compounds, and biological structures. In addition, linear and cyclic chains of molecules have been suggested as dominant structures in liquid water.¹⁶ Chain hexamers are also optimized in this work, starting from the configuration where six oxygen and seven hydrogen atoms are positioned alternately along a line. The remaining five hydrogens are placed on both sides of this line in the same plane, and at 0.957 Å (the O–H distance in an isolated water molecule) from the corresponding oxygen atoms. The structures of clusters are optimized using the GIPAW pseudopotentials and allowing all atoms to relax. Then the ground-state and NMR calculations are carried out. Seven ¹⁶O hexamers, as well as the same clusters where all oxygen nuclei are replaced with ¹⁷O isotopes, are studied. The isotopic substitution enters into the calculation from oxygen pseudopotential files where nuclear masses are present. This produces small variations in bond lengths and angles between optimized ¹⁷O and ¹⁶O clusters, but global symmetries of clusters are preserved. Small initial local variations of atomic positions produce differences in NMR parameters between ¹⁷O and ¹⁶O clusters.

3. Results and Discussion

Optimized structures of water hexamers are presented in Figure 1 and Figure 2. Clusters with ¹⁷O and ¹⁶O nuclei show the same global morphology, whereas the bond distances and angles in corresponding isomers are slightly different. These structures, optimized using the GIPAW pseudopotentials, are in good agreement with other calculations which have been carried out by applying various exchange functionals and corresponding pseudopotentials, as well as by using different atom-centered basis sets and corresponding approximations.^{2–8} A single water molecule is also studied using the same GIPAW pseudopotentials. It is calculated that the O–H distance is 0.975 Å and the H–O–H angle is 103.7°. In a comparison, the DFT GGA calculation with the PBE functional and norm-conserving pseudopotentials has produced 0.972 Å and 104.2° as corresponding values.^{28,43} The experimental data for an isolated water molecule are 0.957 Å and 104.5°. A calculated distribution of the energies above the minimum for all isomers is shown in Table 1. In simulations of water hexamers different isomers have been calculated as the most stable.^{2–7} For example, Table 2 in ref 4 shows that only the bag and cyclic isomers have not been found as the most stable by any of several methods that have been used in recent computational and experimental studies. However, differences in energy among isomers are small. Exceptions are chain isomers. These structures are stable in the GIPAW method (as well as in other calculations^{8,9}), but their energies are substantially higher when compared with other hexamers studied here.

The values of 315.8 ppm for ¹⁷O and 30.96 for ¹H absolute chemical shifts are obtained here for the water monomer using the GIPAW model. The Hartree–Fock method yielded a similar value of 30.86 ppm for the hydrogen shift, when the H atom was taken as the gauge origin.⁴⁴ A recently revised suggested absolute value for the ¹⁷O chemical shift is 287.5 ppm for bulk liquid water and 323.6 ppm for gas water.⁴⁵ The reference value for the ¹H shift obtained from the multiconfigurational self-consistent field calculations for the gas water phase is 30.47

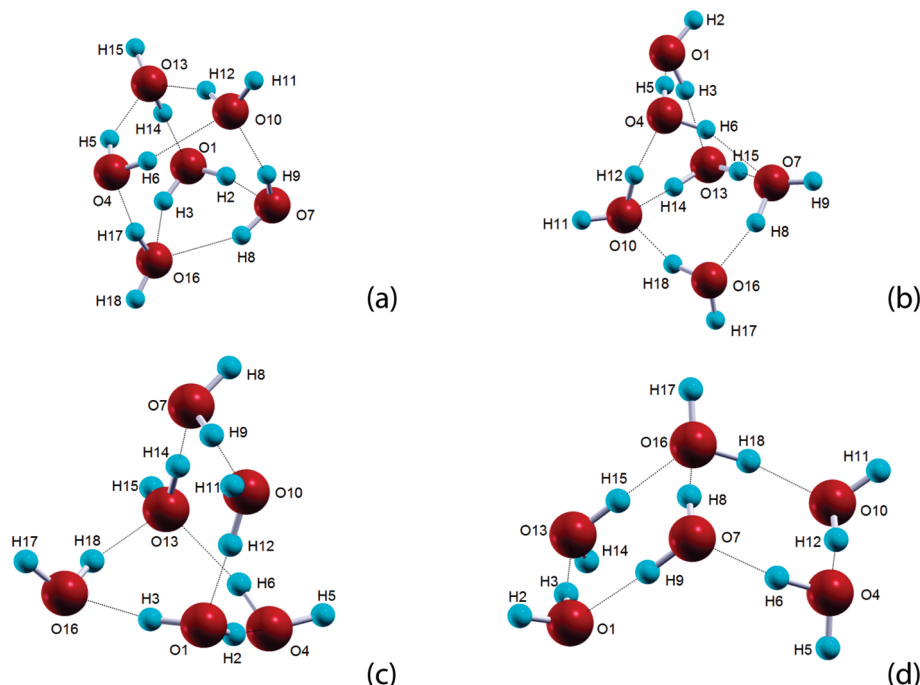


Figure 1. Structures of water hexamers: (a) prism, (b) cage, (c) bag, and (d) book. The dotted lines represent H bonds. The labeling scheme for oxygen and hydrogen atoms is also shown. These images are produced using the XCrySDen package.⁴²

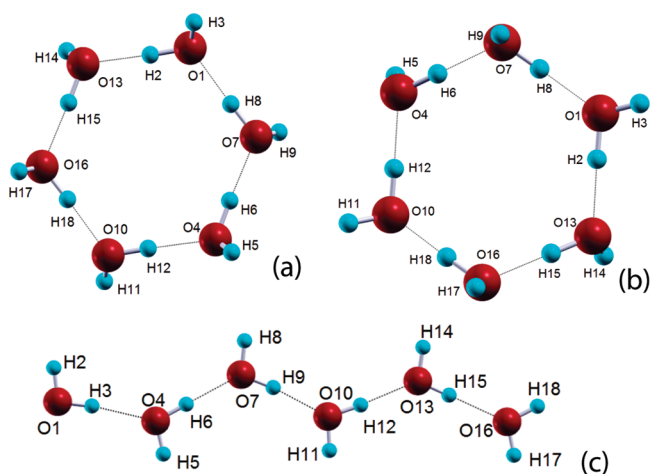


Figure 2. Structures of water hexamers: (a) cyclic I, (b) cyclic II, and (c) chain.

TABLE 1: Energies of Water Hexamers in the GIPAW Model (Relative to the Minimum Energy of Corresponding Isomers)

¹⁶ O clusters	ΔE (kcal/mol)	¹⁷ O clusters	ΔE (kcal/mol)
prism	1.10	prism	1.00
cage	1.04	cage	0.72
book	1.51	book	
bag	2.29	bag	0.85
cyclic I		cyclic I	0.13
cyclic II	2.58	cyclic II	1.19
chain	17.35	chain	18.01

ppm.⁴⁶ The values of oxygen and hydrogen chemical shifts in a water monomer calculated using the Gaussian package, where clusters have been optimized at MP1PW91/6-311+G(2d,p) level and the GIAO method has been applied, are respectively 327.3 and 31.71 ppm.³³ Therefore, in a comparison with reference values for gas water (of $\sigma(^{17}\text{O}) = 323.6$ ppm and $\sigma(^1\text{H}) = 30.47$ ppm), the GIPAW model of a water monomer produces a worse

TABLE 2: Average Relative Hydrogen Chemical Shifts δ

¹⁶ O clusters	δ (ppm)	¹⁷ O clusters	δ (ppm)
prism	3.76	prism	4.53
cage	3.80	cage	4.68
book	3.89	book	4.92
bag	3.80	bag	4.78
cyclic I	4.36	cyclic I	4.77
cyclic II	3.84	cyclic II	4.79
chain	2.83	chain	2.81

value for the ¹⁷O chemical shift and better one for the ¹H shift, than the Gaussian based calculations in ref 33.

Relative chemical shifts in hexamers are shown in Table 2, Table 3, Table 4, Figure 3, and Figure 4. The calculated here absolute shifts for the ¹⁷O water monomer in the GIPAW method are taken as reference values. Table 2 shows the values (averages for all 12 nuclei in a cluster) of the hydrogen chemical shift. The oxygen isotope dependence of ¹H chemical shifts in the (H₂¹⁶O)₆ and (H₂¹⁷O)₆ clusters is obvious. The standard deviations for averages in Table 2 (especially for cyclic isomers) are high. The quasi-planar cyclic isomers are highly symmetric, and their shifts fall into two groups: smaller values for absolute chemical shifts of nuclei which are involved in hydrogen bonding and larger ones for H atoms whose bonds point outside of the ring. Hydrogen chemical shifts in other isomers spread into more values. However, it is also possible in these isomers to distinguish between H-bonded atoms with smaller, and H-nonbonding atoms with larger absolute chemical shifts. Similar behavior has been observed in other calculations.^{32,35} It should be pointed out that relative shifts presented in this work increase when absolute ones decrease. Two examples of a distribution for the values of chemical shifts for all hydrogen nuclei are shown in Figure 3. As presented in Table 2, for the ¹⁶O cyclic I and cyclic II isomers with a similar geometry, variations in the H atom positions around rings produce rather different average values of the hydrogen chemical shift (4.36 ppm vs 3.84 ppm). The average relative hydrogen shifts of chain isomers shown in Table 2 are much smaller, in a comparison with other hexamers. Oxygen chemical shifts are shown in

TABLE 3: Relative Hydrogen Chemical Shifts for All Atoms in ^{17}O Clusters (Prism, Cage, Bag, and Book Isomers)^a

isomer	site	δ (ppm)	isomer	site	δ (ppm)
prism	H2	7.44	bag	H2	5.87
	H3	3.12		H3	5.80
	H5	4.53		H5	0.51
	H6	2.63		H6	5.39
	H8	3.58		H8	0.69
	H9	4.38		H9	10.17
	H11	0.94		H11	0.83
	H12	6.46		H12	10.76
	H14	11.15		H14	10.15
	H15	1.29		H15	1.13
	H17	7.94		H17	0.53
	H18	0.86		H18	5.52
cage	H2	0.63	book	H2	0.62
	H3	7.55		H3	7.25
	H5	7.04		H5	0.80
	H6	3.86		H6	9.80
	H8	8.13		H8	4.01
	H9	1.07		H9	6.98
	H11	1.24		H11	0.77
	H12	10.67		H12	9.92
	H14	3.39		H14	0.71
	H15	4.44		H15	6.99
	H17	0.74		H17	1.13
	H18	7.37		H18	10.06

^a The labeling scheme for hydrogen atoms is shown in Figure 1.

TABLE 4: Relative Hydrogen Chemical Shifts for All Atoms in ^{17}O Clusters (Cyclic I, Cyclic II, and Chain Hexamers)^a

isomer	site	δ (ppm)	isomer	site	δ (ppm)	isomer	site	δ (ppm)
cyclic I	H2	8.81	cyclic II	H2	8.99	chain	H2	-0.73
	H3	0.71		H3	0.59		H3	4.63
	H5	0.71		H5	0.76		H5	0.14
	H6	8.82		H6	9.02		H6	6.49
	H8	8.80		H8	8.70		H8	0.50
	H9	0.72		H9	0.57		H9	6.77
	H11	0.72		H11	0.59		H11	0.55
	H12	8.82		H12	9.11		H12	6.66
	H14	0.71		H14	0.73		H14	0.71
	H15	8.82		H15	9.05		H15	5.58
	H17	0.71		H17	0.57		H17	1.21
	H18	8.85		H18	8.77		H18	1.18

^a The labeling scheme for hydrogen atoms is shown in Figure 2.

Figure 4. In two cyclic isomers, because of their symmetry, shifts are almost the same for all oxygen nuclei. Average values of the ^{17}O relative chemical shift are as follows: 37.3 (prism), 37.3 (cage), 36.0 (bag), 36.7 (book), 31.5 (cyclic I), 32.6 (cyclic II), and 13.9 ppm (chain). Average relative oxygen chemical shifts are much smaller for two chain isomers. In addition, relative shifts for oxygens at both ends of the chains are smaller than for nuclei in the interior of these linear isomers.

Löwdin charges⁴⁷ of hexamers are also analyzed. The average total charges for ^{17}O clusters are from 6.4375 (prism) to 6.4902 (cage). Löwdin charges of hydrogens are from 0.7232 (prism) to 0.7262 (book and chain). Typical average charge transfer to oxygen atoms are 0.44–0.49. As for absolute chemical shifts, the total charge is smaller for H-bonded atoms. The spilling parameter⁴⁸ shows the amount of the total charge lost when the eigenstates from plane-wave calculations are projected on the atomic basis. Therefore, the spilling parameter describes the quality of calculated Löwdin charges. Spilling parameters for

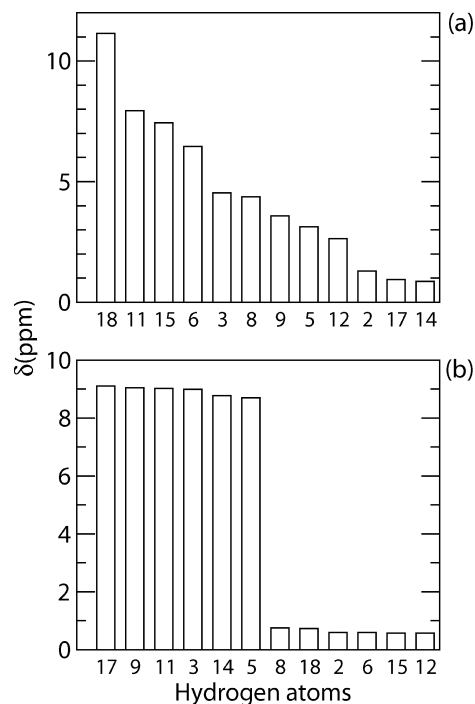


Figure 3. Relative ^1H chemical shifts of all nuclei represented as descending ordered bars (labeled with the hydrogen atom numbers shown in Figure 1a and Figure 2b) for two ^{17}O clusters: (a) prism and (b) cyclic II.

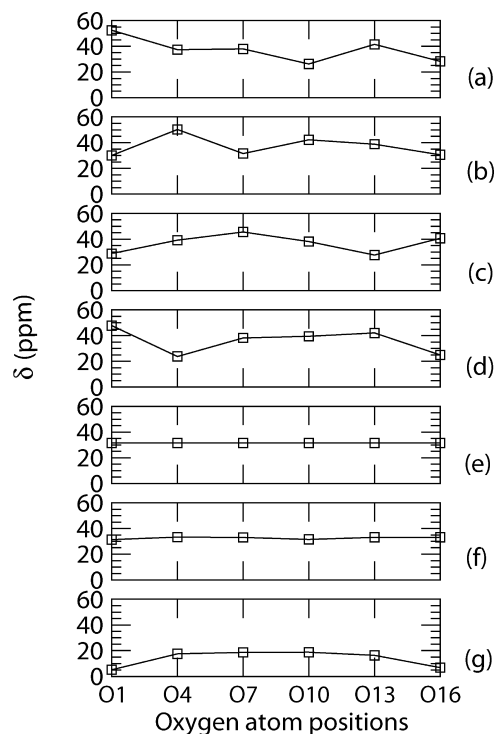


Figure 4. Relative ^{17}O chemical shifts for seven ^{17}O hexamers: (a) prism, (b) cage, (c) book, (d) bag, (e) cyclic I, (f) cyclic II, and (g) chain. The labeling scheme for oxygen atoms is shown in Figure 1 and Figure 2.

calculated hexamers are low: 0.0075 (prism, cage, book, and bag), 0.0076 (cyclic I and cyclic II), and 0.0079 (chain).

The quadrupolar NMR parameters of ^{17}O clusters are presented in Table 5 and Table 6. Values of C_Q (the quadrupolar coupling constant) and η (the asymmetry parameter) for various sites are similar to each other, but fluctuations around the

TABLE 5: Quadrupolar Coupling Constants C_Q and the Asymmetry Parameter η (Prism, Cage, Bag, and Book Isomers)^a

isomer	site	C_Q (MHz)	η	isomer	site	C_Q (MHz)	η
prism	O4	8.43	0.83	bag	O4	8.48	0.79
	O13	9.26	0.79		O13	9.79	0.81
	O10	8.99	0.82		O10	8.88	0.91
	O16	9.52	0.82		O16	8.94	0.91
	O1	8.59	0.95		O1	8.66	0.94
	O7	9.24	0.87		O7	9.75	0.81
cage	O4	9.36	0.86	book	O4	9.35	0.85
	O13	8.34	0.83		O13	8.89	0.92
	O10	9.24	0.86		O10	8.55	0.82
	O16	8.49	0.97		O16	8.85	0.92
	O1	9.13	0.79		O1	9.45	0.84
	O7	9.32	0.85		O7	8.86	0.91

^a The labeling scheme for oxygen atoms is shown in Figure 1.

TABLE 6: Quadrupolar Coupling Constants C_Q and the Asymmetry Parameter η (Cyclic I, Cyclic II, and Chain Hexamers)^a

isomer	site	C_Q (MHz)	η
cyclic I	O4	9.35	0.84
	O13	9.36	0.84
	O10	9.38	0.84
	O16	9.37	0.84
	O1	9.36	0.84
	O7	9.37	0.84
cyclic II	O4	9.45	0.84
	O13	9.29	0.85
	O10	9.29	0.87
	O16	9.45	0.84
	O1	9.27	0.85
	O7	9.29	0.87
chain	O4	10.37	0.77
	O13	10.40	0.74
	O10	10.44	0.74
	O16	10.48	0.73
	O1	10.65	0.71
	O7	11.37	0.66

^a The labeling scheme for oxygen atoms is shown in Figure 2.

averages are apparent. The quadrupolar coupling constants are in the range from 8.34 to 11.37 MHz. Average values of C_Q are as follows: 9.01 (prism), 8.98 (cage), 9.08 (bag), 8.99 (book), 9.37 (cyclic I), 9.34 (cyclic II), and 10.62 MHz (chain). The values of η are in the range from 0.66 to 0.97. Average values of η are as follows: 0.85 (prism), 0.86 (cage), 0.86 (bag), 0.88 (book), 0.84 (cyclic I), 0.85 (cyclic II), and 0.73 (chain). Experimental values for ^{17}O quadrupole parameters in bulk water are $C_Q = 10.175$ MHz and $\eta = 0.75$.⁴⁹ Therefore, the confinement of water molecules causes a decrease of the quadrupolar coupling constant and an increase of the asymmetry parameter in more stable hexamers. An exception is the chain isomer, where an opposite trend is found. Although experimental methods cannot provide the sign of the quadrupolar coupling constant, the GIPAW model used here (for the nuclear quadrupolar momentum of oxygen $Q = -25.58 \times 10^{-31} \text{ m}^2 \text{ s}^{-1}$) gives the positive C_Q for all nuclei and in all hexamers.

4. Conclusions

NMR parameters of ^1H , ^{16}O and ^{17}O nuclei in the prism, cage, bag, book, chain, and two cyclic isomers of ^{16}O and ^{17}O water hexamer clusters are studied using the GIPAW method within the pseudopotential density functional theory. The hydrogen and oxygen chemical shifts, as well as quadrupolar coupling

constants and asymmetry parameters, are calculated. It is found that NMR parameters depend on the geometry of the isomer and the position of a nucleus in the cluster. The values of chemical shifts are considerably different even for two cyclic hexagonal forms. For six more stable hexamers differences among their average chemical shifts up to 0.6 ppm for H and up to 5.8 ppm for the ^{17}O nuclei are calculated. However, relative shifts are much smaller (or absolute shifts are much bigger) for less stable chain isomers. For more stable hexamers quadrupolar asymmetry parameters increase and coupling constants decrease when compared with bulk water, whereas the chain hexamer shows an opposite behavior. Values of NMR parameters in water hexamers shed light on local properties and possible fluctuations of NMR parameters in bulk H_2O . Two hydrogen-bonded configurations have been proposed in recent studies of the structure of liquid water. This is in contrast to the generally accepted model of tetrahedral coordination of water molecules. A chain hexamer in the GIPAW model studied here is substantially less stable than other isomers. The values of NMR parameters of the chain suggest that this hexamer is not a typical local structure in bulk water. If used with good quality pseudopotentials, GIPAW is an efficient method for future studies of NMR parameters in aqueous nanoparticles and bulk. For example, GIPAW is suitable for computational NMR studies of large hydrated biological systems.

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