Effect of the Silyl Substitution on Structure and Vibrational Spectra of Hydrogen-Bonded Networks in Dimers, Cyclic Trimers, and Tetramers

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Geometries of the hydrogen bound clusters $(ROH)_n$ ($n = 1-4$, R = H, CH_3, and SiH_3) are optimized at the B3LYP/DZP+diff level of theory. The reliability of the theoretical method employed for the description of the electronic structure of the hydrogen-bonded network is assesed by a comparison of the predicted geometry parameters and the BSSE corrected association energies with the existing experimental parameters and the higher level theoretical estimates for a water dimer and methanol oligomers. Cyclic structures with S_4 symmetry, similar in the hydrogen-bond arrangement to that of the water tetramer, were found as minima at the potential energy surface of methanol and silanol tetramers. The cyclic silanol trimer has the C_{3h} symmetry, in contrast to water and methanol trimers which are characterized by the nonplanar asymmetric structures. The O−O atomic separations decrease and association energies per monomer increase with n and in going from H to SiH_3. The silanol tetramer has the highest association energy per monomer among the analyzed systems. This finding is in keeping with the dominance of tetrameric cyclic structures in the experimentally studied crystal structures of silanols. Vibrational frequency shifts with n in the water−methanol−silanol systems are discussed and frequencies for methanol and silanol trimers and tetramers are predicted from the ab initio force fields scaled with factors refined to fit experimental vibrational frequencies of monomers and a water dimer. The main feature of the frequency change with n, along with the lowering of the OH stretch, is the upward shift of the OH bend, which is exceptionally high in silanols.

Introduction

The formation of inorganic networks containing SiO bonds has gained much attention in the past years, because this process is widely used for the fabrication of inorganic materials (ceramics, glasses, fine monodisperse powders, films, and fibers) with desired shape and properties. The precursors of this process (known as a sol−gel process) are halo- and alkoxysilanes which undergo hydrolysis (as a first step) with the subsequent condensation of silanols and formation of monolithic inorganic gels at low temperatures.[1] Thus, silanols are important intermediates in this process of high practical importance, and the knowledge of their structure and vibrational spectra may give a further insight into the interpretation of experimental results on sol−gel processes.

However, the experimental study of silanols is hindered by their instability toward condensation. The simplest silanol H_3SiOH was not isolated and characterized experimentally, but theoretical predictions of its structure and the vibrational spectrum exist.[2−11] The steric hindrance produced by the bulkier substituents at silicon prevents the rapid condensation and allows structural characterization of the silanol structure in the solid state by X-ray diffraction. With one exception of the specific substituent,[12] silanol molecules in condensed phases exhibit different motifs of hydrogen bonded associates and frameworks as shown by the X-ray and vibrational spectroscopy studies.[13] Within the scope of the reported silanol oligomer structures, the predominant pattern of the hydrogen bonded aggregates of monofunctional silanols is that of the tetrameric cycles. Crystal structures containing tetramers include t-Bu_2FSiOH,[14] t-Bu_2HSiOH,[15] and Ph_3SiOH.[16] However, sterical hindrance of substituents in the more crowded silanols prevents formation of tetramers, and, as a result, the dimers are formed.[17−18] Because vibrational spectroscopy is a regular tool for the monitoring of sol−gel processes, the knowledge of vibrational spectra of individual silanols and the frequency changes in the process of their condensation may be very helpful for the experimental research. However, to the best of our knowledge, experimental vibrational spectra are known only for a few silanols; the most complete experimental spectral data exist for trimethylsilanol.[19−22]

In contrast to the absence of both experimental and theoretical data on silanol oligomers, there exist numerous studies of water dimers, trimers, and tetramers.[23−74] Studies of the methanol clusters are less abundant, but these species received considerable attention in recent years.[75−94] To the best of our knowledge, there are only two works on silanol dimers.[8,75] Because silanols are stronger acids than the corresponding carbinols and their basicity does not differ significantly from carbinols,[95−98] one may expect stronger hydrogen bonding in silanol oligomers. However, no quantative estimates of this difference for silanol clusters higher than dimers were reported.

Theoretical Methods

State-of-the-art quantum chemical methods applied extensively for water clusters are too computationally demanding to be used for methanol and especially silanol clusters. DFT

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methods provide a reasonable compromise between the accuracy of calculations and computational costs. Extensive application of DFT methods to numerous chemical problems including hydrogen bonding has shown that hybrid DFT methods, especially B3LYP, perform well in the prediction of the properties of hydrogen bonded systems.[46−54] The computational method employed in this work was the hybrid DFT method combining Becke's three parameter exchange functional[99] with the LYP correlation functional[100] (B3LYP) as implemented in the Gaussian 98 program.[101] The basis set was constructed from the double-ζ set of Huzinaga et al.,[102] namely, Si (11s7p/6s4p), C, O (9s5p/4s2p) H (4s/2s). This basis set was augmented with one set of *d* polarization functions with [$\alpha_d(Si) = 0.5$, $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$] and *p* polarization functions at H [$\alpha_P(H) = 0.75$], as well as one set of diffuse functions for H, C, and O [$\alpha_s(H) = 0.048273$, $\alpha_P(C) = 0.034$, and $\alpha_P(O) = 0.059$]. This basis set is designated as DZP+diff.

The "tight" option as a criterion for optimization was used in Gaussian, and in some cases, in which the low accuracy of the default integration grid prevented the B3LYP optimization convergence and/or calculated vibrational frequencies were very low (below 10 cm^{-1}), the larger integration grid of 99 radial shells and 434 angular points in each shell (99434) was used. All structures were fully optimized and vibrational frequencies were evaluated for all stationary points. Basis set superposition error corrections for trimers and tetramers are estimated as proposed by Nielsen et al.[35] Scaling of the ab initio force fields in natural internal coordinates was performed as this procedure is implemented in the MOLVIB program.[103]

Results and Discussion

A. Dimers. The water dimer is one of the most studied hydrogen bonded systems, both theoretically and experimentally. The available experimental data, i.e., the oxygen−oxygen intermolecular distance and the binding energy, allowed theoretical chemists to check the performance of different methods in the reproducibility of the properties of the hydrogen bonded systems. The most accurate CCSD(T) estimates of r_eO−O are 2.895 Å with the aug-cc-pVTZ basis set[33] and 2.909 Å with the TZ2P(d,f)+diff set.[40] These results are still significantly lower than the generally accepted r_eO−O value of 2.952 Å derived from the experimental r_0 values of Odutola and Dyke[60] and corrected for the anharmonicity effects by van Duijneveldt-van de Rijdt and van Duijneveldt.[26] This systematic underestimation of the O−O separations by the most accurate methods is substabtially diminished at the methods which use the BSSE corrected geometry optimization procedure (2.925[34] and 2.917 Å[36]). However, in a recent work by Mas et al.,[62] a new experimental/theoretically corrected value of 2.910 Å was recommended. This value is in excellent agreement with theoretical predictions of Tschumper et al.[40] but makes BSSE corrected results somewhat overestimated. Other methods (mostly different versions of MP2) predict the r_eO−O value in the 2.891−2.953 Å range (see Table 1 of ref 38). Our B3LYP result (2.891 Å) is close to the MP2 predictions with similar basis sets and lies at the lower boundary of this range.

TABLE 1: Association Energies and BSSE Corrections (kcal/mol) of Water, Methanol, and Silanol Oligomers Estimated at the B3LYP/DZP+diff Level of Theory ($\Delta E_0 = \Delta E_e + \Delta$ ZPVE, $\Delta H_{298} = \Delta E_e + \Delta$ THERM)

oligomers	ΔE_e	ΔE_0	ΔH_{298}	BSSE corr.	ΔH_{298}^{corr}	ΔH_{298} (exp)	$-\Delta H_{298}^{corr}/n$[a]
$(H_2O)_2$	−5.7	−3.5	−4.0	0.2	−3.8	−3.6[b]	1.9
$(H_2O)_3$	−17.3	−11.6	−13.5	1.6	−11.9		4.0
$(H_2O)_4$	−31.4	−22.7	−25.7	2.6	−23.1		5.8
$(CH_3OH)_2$	−5.8	−4.4	−4.1	0.5	−3.6	−3.2[c]	1.8
$(CH_3OH)_3$	−17.1	−13.5	−13.6	1.4	−12.2	−12.5[d]	4.1
$(CH_3OH)_4$	−30.9	−25.5	−25.7	2.7	−23.0	−24.2[c]	5.8
$(SiH_3OH)_2$	−6.0	−4.6	−4.4	0.4	−4.0		2.0
$(SiH_3OH)_3$	−18.3	−15.1	−15.0	1.5	−13.5		4.5
$(SiH_3OH)_4$	−31.9	−26.8	−26.	3.0	−23.8		6.0

[a] The BSSE corrected binding enthalpy per monomer. [b] Reference 59. [c] Reference 106. [d] Reference 105.

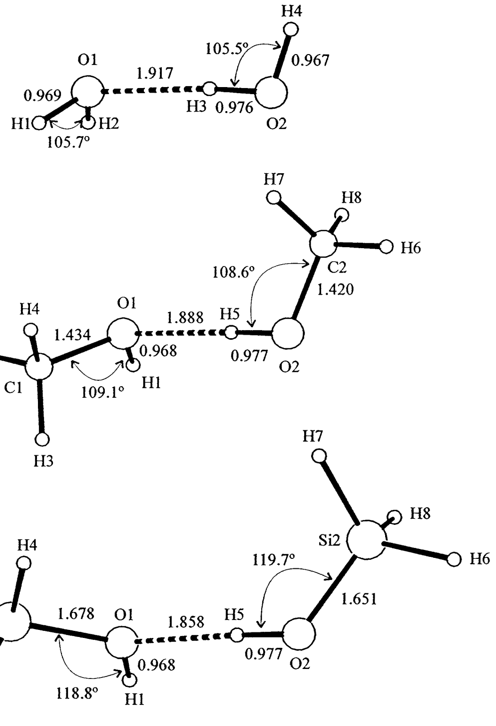

Figure 1. Equilibrium B3LYP/DZP+diff structures of global minima for water, methanol, and silanol dimers.

The experimental estimate of the binding enthalpy at 373 K (ΔH_T) is 3.6 ± 0.5 kcal/mol[59] that corresponds to the ΔE_e value of 5.4 kcal/mol. The best theoretical prediction of this value is 5.0 kcal/mol.[38] Our B3LYP estimate of the ΔE_e value (5.7 kcal/mol) after corrections for the basis set superpositions error (BSSE) with the counterpoise method[104] is in excellent agreement with experiment (Table 1). However, this agreement between experimental binding energies and those predicted by B3LYP with the double-ζ quality basis sets may be fortuitous, because, as was noticed by González et al.,[46] the increase in the quality of the basis set from 6-31+G(d,p) to 6-311+G(3df,-2p) results in larger deviations. Nevertheless, the comparison of our B3LYP results for the hydrogen bonded water dimer with experimental thermochemical parameters and those obtained by the more accurate methods, ascertains that B3LYP/DZP+diff gives satisfactory results in the description of hydrogen bonded systems at much lower costs than those of MO correlated methods.

The water dimer, which is formed by hydrogen bonding between the hydrogen atom of the proton donor molecule and the oxygen atom of the proton acceptor, belongs to the point group C_s. Similar arrangements of atoms were found as energy minima for methanol[8,75−77] and silanol[8,75] dimers (Figure 1). However, the structure of the silanol dimer differs from the analogous dimers by the mutual orientation of the hydrogen bound molecules (Figure 1). This difference manifests itself in the change of the equilibrium XOOX torsion angle: in water and methanol (X = H and C), dihedral angles are nearly equal

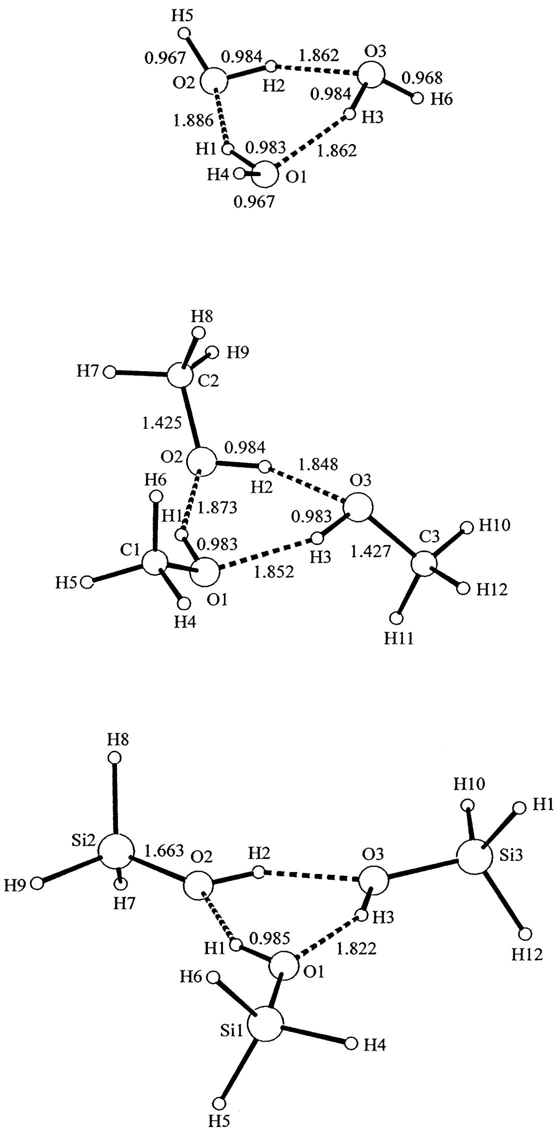

Figure 2. Equilibrium B3LYP/DZP+diff structures of global minima for water, methanol, and silanol trimers.

and close to 120° (119.8 and 120.9°), whereas in silanol, this dihedral angle becomes close to 90° (96.8°).

B. Trimers. Although the water trimer is not so well-characterized by experimental methods as the water dimer, there exist experimental[58,66] and quantum-chemical studies of the water trimer.[27−31,35,44−45] It was found that the global minimum corresponds to the cyclic structure with the nearly planar arrangement of the hydrogen-bond network and three exocyclic OH bonds, two of which are above this plane and one is below. Similar structure was obtained in this work (Figure 2). The structure possesses C_1 symmetry; however, two O−O distances are nearly equal, whereas the third O−O separation (between oxygens with exocyclic hydrogens above the plain) is substantially longer.

The analysis of the vibration−rotation tunneling spectroscopy data on the $(D_2O)_n$ clusters[58] confirmed the cyclic structure of the water trimer and refined O−O separations. Values of 2.97 and 2.94 Å were obtained in this study. However, these values are not very accurate, because of the lack in the experimental data, some constraints should be used for their derivation. The more rigorous treatment yielded the 2.84 Å value.[66] The CCSD/aug-cc-pVDZ equilibrium distances of Nielsen et al.[35] (2.835, 2.837, and 2.839 Å) are close to this estimate, whereas CCSD/DZP+diff separations of Fowler and Schaefer[35] (2.850, 2.860, and 2.909 Å) are slightly longer. Our B3LYP/DZP+diff prediction (2.760, 2.762, and 2.769 Å) underestimates O−O separations.

To the best of our knowledge, there is no experimental value for the binding energy of the water trimer. The best theoretical estimate of this value is that of Nielsen et al.[35] The infinite basis set extrapolation of the frozen core MP2 results with taking into account the BSSE, core correlation, and higher order correlation effects gave the value of 15.9 ± 0.2 kcal/mol. Our BSSE corrected ΔE_e value, that is, 15.7 kcal/mol (ΔE_e + BSSE corr. of Table 1), is in a good agreement with this estimate.

The cyclic structure was also found to be the global minimum at the potential energy surface of the methanol trimer.[77−80] Similar to the water analogue, it has no symmetry and the hydrogen bonded ring is characterized by the two nearly equal short O···H separations and the one which is longer. The geometry optimized in our work (Figure 2) slightly differs from other B3LYP studies, in which 6-311+G(d,p)[77] and 6-31+G-(d)[78] were employed. Our geometry is characterized by shorter O···H and O−O separations. This differences may be due to the presence of diffuse functions on hydrogens in our set.

Association enthalpy of the methanol trimer was estimated by Mó, Yáñez, and Elguero[77] as a single point calculation with a larger basis set augmented with diffuse functions on H [6-311++G(3d,2p)] to be 9.2 kcal/mol. It is substantially lower than the experimental estimate of 12.5 kcal/mol.[105] Our ΔH_{298} value is closer to experiment (Table 1). The difference between our results and those of Mó et al.[77] may stem from the underestimation of the strength of the hydrogen bond in the 6-311+G(d,p) set at which the geometry was optimized in the latter study.

There are no previous reports of the structure of the silanol trimers. Optimization of this structure in this work started from the geometry similar to that of the cyclic methanol trimer. However, the energy minimum found for the silanol trimer possesses the C_{3h} symmetry with three SiO bonds coplanar with the hydrogen-bond ring, in contrast to the asymmetric methanol analogue (Figure 2). The O−O interatomic separations in the planar hydrogen-bonded ring of silanols is considerably shorter than those of methanol (Table 2). The increase in the hydrogen bonding manifests itself also in the growth of the association energy from 12.2 kcal/mol for methanol to 13.5 kcal/mol for silanol (BSSE corrected ΔH_{298} values, Table 1).

C. Tetramers. All previous ab initio calculations of the water tetramer[23−25,27−29,42,47] revealed the cyclic S_4 structure as a global minimum of the system. The structure of the global minimum for the methanol tetramer was found to have a cyclic S_4 structure, similar to the water tetramer (Figure 3).[78,90] Though in both studies of the methanol tetramer the B3LYP method was used, O−O separations reported differ substantially. Hagemeister et al.[78] employed the 6-31+G(d) basis set and obtained 2.737 Å for the equilibrium O−O distance, whereas the Vener and Sauer[90] optimized value with the modified DZP basis set (triple-ζ in the valence region of oxygen) is 2.674 Å. Our equilibrium value lies between these two, i.e., 2.702 Å (Table 2). The experimental estimate of the binding enthalpy of the gaseous tetrameric clusters of methanol, that is, 24.2 kcal/mol,[106] is close to our BSSE corrected ΔH_{298} value of 23.0 kcal/mol (Table 1).

The similar cyclic S_4 structure was found in this work as a minimum at the $(SiH_3OH)_4$ potential energy surface. The silanol tetramer is characterized by the further decrease of the O−O interatomic separations. This substantial increase not only in

TABLE 2: Equilibrium Geometry Parameters (Bond Lengths in Å; Bond Angles in Degrees) of Methanol and Silanol Clusters $(XH_3OH)_n$ (X = C and Si, n = 1−4) Optimized at the B3LYP/DZP+diff Level of Theory

n	parameters	X = C	X = Si	n	parameters	X = C	X = Si
1	r OH	0.967	0.966	1	ϕ XOH	108.8	119.5
	r XO	1.427	1.662		ϕ OXH(g)^a	106.7	105.9
	r XH(g)^a	1.095	1.476		ϕ OXH(t)^b	112.2	111.6
	r XH(t)^b	1.102	1.486		τ H(t)^b−X−O−H	−61.5	−60.4
2	r O1−H1	0.968	0.968	2	ϕ O1−X1−H3	111.8	110.7
	r O2−H5	0.977	0.977		ϕ O1−X1−H4	106.7	105.1
	r O1−O2	2.864	2.834		τ H2−X1−O1−H1	−61.7	−60.1
	ϕ O1−H5−O2	177.8	176.8		τ H3−X1−O1−H1	61.2	60.6
	τ X1−O1−O2−X2	−120.9	−96.8		τ H4−X1−O1−H1	179.8	−179.6
	ϕ X1−O1−H1	109.1	118.6		r X2−H6	1.096	1.479
	ϕ X2−O2−H5	108.6	119.7		r X2−H7(H8)	1.103	1.489
	r X1−O1	1.434	1.678		ϕ O2−X2−H6	107.5	106.8
	r X2−O2	1.420	1.651		ϕ O2−X2−H7(H8)	112.4	112.2
	r X1−H2	1.099	1.483		τ H6−X2−O2−H5	179.5	179.4
	r X1−H3	1.100	1.482		τ H7−X2−O2−H5	60.7	59.8
	r X1−H4	1.094	1.475		τ H8−X2−O2−H5	−61.8	61.1
	ϕ O1−X1−H2	111.4	110.3				
3	r O1−H1(H3)	0.983	0.985	3	r X1(X2)−H4(H7)	1.095	1.478
	r O1−H2	0.984	0.985		r X1(X2)−H5(H9)	1.102	1.484
	r O1(O2)−O3	2.754	2.718		r X1(X2)−H6(H8)	1.101	1.484
	r O2−O3	2.765	2.718		ϕ O1(O2)−X1(X2)−H4(H7)	107.5	105.8
	ϕ O1−H1−O2	149.4	149.6		ϕ O1(O2)−X1(X2)−H5(H9)	111.4	111.3
	ϕ O2−H2−O3	151.7	149.6		ϕ O1(O2)−X1(X2)−H6(H8)	112.1	111.3
	ϕ O3−H3−O1	151.2	149.6		ϕ O1(O2)−X1(X2)−H4(H7)	107.5	105.8
	ϕ H1−O2−H2	88.8	90.4		ϕ O3−X3−H10	107.5	105.8
	ϕ H2−O3−H3	88.9	90.4		ϕ O3−X3−H11	111.9	111.3
	ϕ H3−O1−H1	89.8	90.4		ϕ O3−X3−H12	111.4	111.3
	τ H1−O1−O3−O2	−2.4	0.0		τ H4−X1−O1−H1	−178.2	−180.0
	τ H2−O2−O1−O3	1.2	0.0		τ H5−X1−O1−H1	63.2	60.6
	τ H3−O3−O2−O1	−1.4	0.0		τ H6−X1−O1−H1	−59.1	−60.6
	τ X1−O1−O2−O3	−52.0	0.0		τ H7−X2−O2−H2	−177.8	−180.0
	τ X2−O2−O3−O1	−49.8	0.0		τ H9−X2−O2−H2	63.6	60.6
	τ X3−O3−O1−O2	57.6	0.0		τ H8−X2−O2−H2	−58.5	−60.6
	r X1(X2)−O1(O2)	1.425	1.663		τ H10−X3−O3−H3	177.5	180.0
	r X3−O3	1.427	1.663		τ H11−X3−O3−H3	58.2	60.6
	r X1(X2)−H4(H6)	1.095	1.478		τ H12−X3−O3−H3	−63.9	−60.6
4	r OH	0.993	0.995	4	r XO	1.426	1.666
	ϕ OHO	167.8	167.0		ϕ XOH	109.4	119.6
	ϕ HOH	102.0	101.5		r XH(g)^a	1.096	1.479
	τ HOOO	4.0	18.7		r XH(t)^b	1.100	1.484
	τ XOOO	116.7	134.6		ϕ OXH(g)^a	107.8	105.9
	r OO	2.702	2.678		ϕ OXH(g)^a	111.6	111.2

[a] The XH bond which is in the *gauche* position to the oxygen lone pairs. [b] Two XH bonds which are in the *trans* positions to the oxygen lone pairs.

the absolute stability but in the per monomer binding energy may be the reason of the dominance of the tetrameric pattern observed in the solid state. There are no experimental evidences of silanol trimers, whereas tetrameric structures were characterized by the single-crystal X-ray structure analysis to be the building blocks of the *t*-Bu_2HSiOH,[14] Ph_3SiOH,[15] and *t*-Bu_2FSiOH[16] crystal structures. The O−O interatomic distances found in two of these works (2.637−2.684[15] and 2.701 Å[14]) agree well with our predicted value for the H_3SiOH tetramer (2.678 Å). The crystal structure of *t*-Bu_2FSiOH contains longer O−O separations (2.756 Å[16]), but elongation of these distances may be caused by the presence of fluorine as a substituent at Si, which is able to interact repulsively with the hydrogen bond ring oxygens.

D. Trends in Geometries and Binding Energies of Clusters $(RHO)_n$ in Going from R = H to SiH_3. Cooperative effects in the cyclic hydrogen bonded clusters which manifest in a systematic contraction of the O−O separation with increasing cluster size are well-known.[27−29,47,64−66] These effects may stem from the charge-transfer phenomena: in cyclic structures, each molecule is a donor and acceptor of charge transferring in hydrogen bonding. This minimizes the destabilizing effect of the charge transfer to the antibonding orbitals of an acceptor. Other manifestations of these cooperative effects studied both theoretically and experimentally on water clusters include the increase of the binding energy per monomer with cluster size, the linearization of the hydrogen bond O···H−O angles, and the different arrangement of the exocyclic free OH bonds for odd and even n.[27−29,64]

However, these effects are close to saturation in the cyclic tetramers. As shown by Lee et al.,[29] the growth of the water clusters beyond $n = 4$ leads to considerably smaller increments of the binding energy per water monomer. Moreover, among these clusters those with n divisible by four, i.e., with $n = 8$, 12, 16, etc., are the most stable. These structure with “magic” numbers are built from the nearly planar four-membered OH rings. There are also experimental evidences which indicate that the structure of the water hexamer is a cage rather than a ring.[107,108] This “magic” character of the cyclic hydrogen bonded tetramers probably stems from the fact that the H···O−H angle strain in tetramers is minimal, whereas the energy gain, because of the complex formation, is close to saturation. The preference

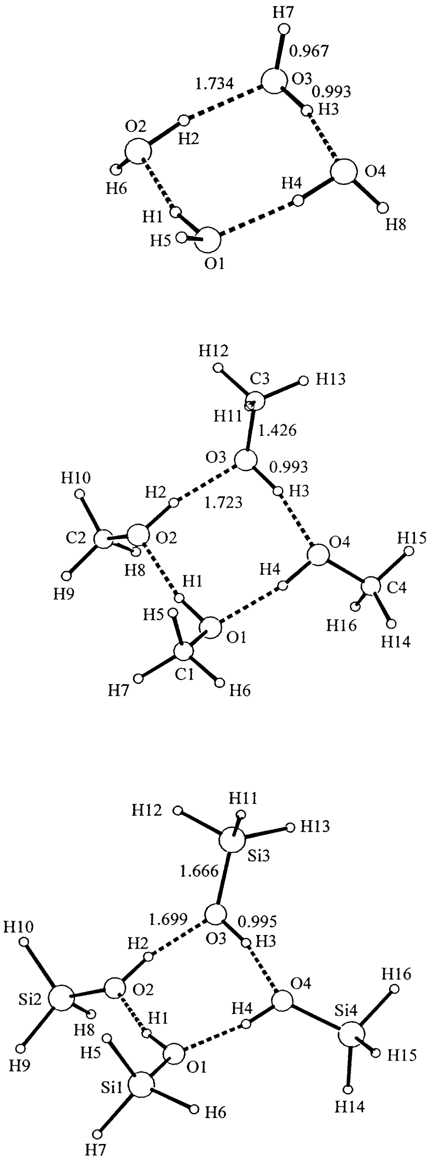

Figure 3. Equilibrium B3LYP/DZP+diff structures of global minima for water, methanol, and silanol tetramers.

of tetrameric structures is supported by the fact that the only cyclic clusters detected experimentally in the methanol gas phase[105] and in the carbinol[106] and silanol[14−16] crystals are cyclic tetramers.

All hydrogen bonded systems considered in this study exhibit the tendency of the hydrogen bond strengthening with the cluster size. Although the predicted contraction of the O−O distance in going from $n = 2$ to 4 decreases in the water−methanol−silanol series (0.181−0.162−0.156 Å), the silanol tetramer possesses the shortest O−O separation among the studied systems, which is by 0.032 Å shorter than in water and by 0.024 Å than in methanol.

The association energies of the clusters follow the geometrical tendencies, although they are more smooth. Thus, the per monomer $\Delta H_{298}^{\mathrm{corr}}/n$ values are almost identical for water and methanol clusters with the same n but slightly increase for silanol. The more pronounced increase of $\Delta H_{298}^{\mathrm{corr}}/n$ is predicted for the silanol trimer (Table 1). This effect may stem from the highly symmetric structure found for this species.

E. Vibrational Spectra. Vibrational spectroscopy provides one of the most important tools for the identification of the hydrogen-bonded clusters. The systematic strengthening of the hydrogen bond with the cluster size manifests in a red shift of the hydrogen-bonded stretch frequencies. This effect for water clusters was numerously studied both experimentally and theoretically[27−29,64−74] and less extensively for those of methanol.[77−79,85,86,90−92] To the best of our knowledge, there are no studies of the vibrational frequency shifts in silanol clusters.

When comparing experimental and theoretically predicted frequencies of vibrations involving hydrogens, one should take into account that the main factor of their discrepancy is not the drawbacks of the quantum chemical approximation but rather the fact that theoretical frequencies are harmonic ones. Usually in the discussion of the spectral changes upon cluster formation, vibrational frequency shifts size are used to avoid this discrepancy. Because one of the aims of this work is the prediction of frequency changes in silanol clusters, we propose an alternative approach, i.e., the use of the force field scaling procedure.[110] When cautiously used (the transfer of scale factors refined for fragments), this empiric procedure may have a predictive power.

Frequencies of vibrational fundamentals of the water molecules in the dimer were identified in the infrared spectroscopy studies in the gas phase[67−69] and in the N_2,[70,72,74] Ar,[70,73] and Ne[71] matrixes. The frequencies of fundamentals of the water dimer trapped in solid neon[71] are closer to the positions of gas-phase absorptions than those in the heavier rare-gas matrixes and, especially, in the nitrogen matrix. However, the study in the Ar[70] matrix provides the most full data on the vibrational frequencies including D_2O and HDO isotopomers. This is the reason these data were used for the scaling of the B3LYP/DZP+diff force field in this work. The results of this scaling are summarized in the Table 3. Because scaling factors used to fit experimental frequencies mainly include anharmonic corrections, it is natural to suppose that these corrections are different for free and H-bonded OH bonds. Therefore, we introduced independent scaling constants for each type of the OH bond. The refinement of three scale factors to fit 18 experimental frequencies of the intramolecular water vibrations (no reliable frequencies of the intermolecular vibrations are reported) in the three isotopomers of the dimer gave the 0.907 scale factor for the nonbonded OH stretch and 0.951 for the H-bonded one. The scale factor for the HOH deformation is 0.975. The intermolecular coordinates corresponding to the low-frequency vibrations were not scaled.

The transfer of these factors to the theoretical force fields of the water trimer and tetramer allowed us to predict experimental (anharmonic) frequencies of these species. They coincide well with experimental vibrational frequencies for H_2O, D_2O, and HDO observed in the Ar matrix[70] and assigned to trimers and multimers (Table 3). However, there is a certain underestimation of the frequencies of ν_1 fundamentals in trimers, especially in the deuterated species.

The scaling factor for the H-bonded OH stretch (0.951) obtained for the water dimer is transferred to the methanol B3LYP force field. Other scaling factors for methanol are refined on the basis of experimental vibrational frequencies of CH_3OH and CD_3OD.[111] Experimental frequencies of the OH stretches of the methanol dimer[91] and trimer[92] were obtained by Huisken et al. employing molecular beam depletion spectroscopy. Two bands for the methanol dimer and three bands for the methanol trimer have been identified in these studies (Table 5). Perchard and Mielke[93] reported frequencies of OH stretching, OH bending, and one of the intramolecular vibrations for various isotopomers of the methanol dimer obtained in a

TABLE 3: Observed and Theoretical (B3LYP/DZP+diff) Vibrational Frequencies (cm^{-1}) of Water Oligomers

	H_2O					D_2O		HDO (D donor)	
				ν_{exp}			ν_{exp}		ν_{exp}
assignment	ω_{theor}	$\omega_{exp}{}^{a}$	$\nu_{sc}{}^{b}$	gas[c]	Ar[d]	ν_{sc}	Ar[d]	ν_{sc}	Ar[d]
				Dimer					
ν_3 aceptor	3926	3899	3742	3746	3726	2743	2766	3701	3681
ν_3 donor	3898	3880	3726	3735	3715	2728	2746	3689	3694
ν_1 aceptor	3814	3797	3632		3634	2617	2615	2678	2706
ν_1 donor	3694	3718	3590	3601	3574	2591	2600	2629	2639
ν_2 donor	1644	1669	1619		1611	1182	1189	1386	1398
ν_2 acceptor	1624	1653	1602		1593	1174	1178	1408	1403
				Trimer					
ν_3			3715			2714	2738	3704	
			3714	3726	3700	2712		3704	
			3709			2709	2733	3699	
ν_1			3510	3533	3528	2540	2580	2561	2587
			3498		3516	2532		2551	2577
			3431			2496		2506	
ν_2			1640			1194		1388	
			1614		1620	1179	1183	1382	
			1610		1602	1175		1377	
				Tetramer					
ν_3			3705			2701		3700	
			3704	3714	3690	2700		3699	
			3704			2700		3699	
			3703			2699		3699	
ν_1			3368	3416	3390	2444	2456	2454	2465
			3325		3374	2415		2425	
			3325			2415		2425	
			3215			2338		2348	
ν_2			1670			1212		1396	
			1635			1192		1382	
			1635		1626	1192		1382	
			1618			1184		1369	

[a] Reference 72, estimated from experimental frequencies with harmonic corrections of ref 115. [b] Scale factors for free OH (0.907), H-bonded OH (0.951), and HOH deformation (0.975) are fit to experimental data (18 frequencies) for three isotopomers of the water dimer. [c] In a supersonic molecular beam; ref 68. [d] In Ar matrixes; ref 70.

N_2 and Ar matrixes study. Their proton donor OH stretch frequency (3505 cm^{-1} in N_2 and 3527 cm^{-1} in Ar) differs significantly from the experimental value of Huisken et al.[91] as well as from our theoretical prediction and is much more close to the corresponding frequency of the methanol trimer (Table 5). The reported COH bending frequencies[93] are in a good agreement with our predictions:

	$(CH_3OH)_2$	$(CD_3OH)_2$	$(CH_3OD)_2$	$(CD_3OD)_2$
expt[93]	1401	1365	929	814
	1345	1307	876	786
theory	1403	1372	920	809
	1342	1282	857	772

This indicates that the scaling factor refined for the isolated methanol molecule describes well the bending COH frequencies of the hydrogen-bonded clusters.

The scaling factors for the SiH_3O group of silanols were determined by fitting the theoretical vibrational frequencies to the experimental spectra of SiH_3OCH_3 and SiD_3OCD_3.[112] In this procedure, the scaling factors for the methoxy group internal coordinates (nonredundant sets as defined in ref 110 were used for OCH_3 and $OSiH_3$ groups) are taken from the methanol calculation and fixed. The factor for the silanol monomer OH stretch was also transferred from methanol. However, for OH stretching coordinates involved in hydrogen bonding, the scale factor c_{OH} was transferred from the water dimer, as it was done for the water trimer and teramer as well as for methanol clusters. Thus, all scale factors for silanol were not varied but rather transferred from other molecules, with the exclusion of c_{SiOH}, corresponding to the the SiOH bending coordinate, which cannot be determined in this way.

Fortunately, although the complete experimental vibrational spectrum of the silanol molecule was not reported, there exists an assignment of the SiO stretch of this molecule. Among the IR absorption bands which belong to the photolysis products of the reaction between SiH_4 (SiD_4) and ozone, co-deposited with argon at 17 K, the bands at 859 (SiH_4) and 874 cm^{-1} (SiD_4) were ascribed to vibrations of SiH_3OH and SiD_3OD correspondingly.[113] Two other bands for the species with ^{18}O, i.e., 851 and 850 cm^{-1}, were assigned to $SiH_3{}^{18}OH$ and $SiD_3{}^{18}OD$. The 15 cm^{-1} blue shift of the SiO stretch upon deuteration may be explained by the fact that in SiH_3OH this stretch is perturbed and shifted down by the SiOH bend, whereas in SiD_3OD, this coupling disappears because of the lowering of the SiOD deformation frequency. Thus, the mode corresponding to the observed band is strongly coupled with the SiOH bend, and therefore, these data allow us to determine the scale factor for the bending coordinate. The best fit to experimental frequencies (with $c_{SiO} = 1.046$ fixed to the value refined for silyl methyl ether) gives $c_{SiOH} = 1.115$:

	(SiH_3OH)	$SiH_3{}^{18}OH$	SiD_3OD	$SiD_3{}^{18}OD$
expt[113]	859	851	874	850
theory	854	827	881	856

The similar harmonic frequencies were found in the CCSD(T)/cc-pVTZ study:[10] 858, 829, 883, and 859 cm^{-1}. The only significant discrepancy between our scaled B3LYP result and that of CCSD, on one hand, and the observed frequencies, on the other, is the overestimation of the red shift of the ν SiO (δ SiOH) band in $SiH_3{}^{18}OH$.

The vibrational spectra of silanol clusters obtained with the scaling procedure described above are shown in the Table 4. Comparing these spectra, one may notice that among the internal vibrations of silanol the δ SiOH mode exhibits the greatest changes with the cluster size in addition to the well-known red shift of the OH stretch (Table 4). The high frequency totally symmetric components of δ SiOH (1272 cm^{-1} in trimer and 1352 cm^{-1} in tetramer) are inactive in the IR spectra. However, the frequencies of δ SiOH degenerate modes for the trimer and tetramer also lie substantially higher than that for the monomer (by 172 and 299 cm^{-1}). Thus the frequency gap between ν SiO and δ SiOH steadily increases in going from the monomer to the tetramer. Therefore, the coupling of the SiO stretch and SiOH bending vibrations, which is inherent to the monomer and partly to the dimer, completely disappears in trimers and tetramers. The scaled values of the IR active tetramer δ SiOH vibrations are 1237 and 1232 cm^{-1} (Table 4). Note, that the tendency for the ROH bending frequency to increase with n may be found for water and methanol oligomers. However, in silanol, the B3LYP/DZP+diff frequency shift (unscaled) is 463 cm^{-1} (from monomer to the high frequency component in tetramer), whereas in the two other systems, they are considerably smaller (116 cm^{-1} for methanol and 75 cm^{-1} for water).

Despite the pronounced dependence of the δ SiOH mode on the cluster size, this feature hardly may be used for the identification of oligomers of the more complex silanols because of contamination of the 1100−1300 cm^{-1} spectral range by the deformation modes of substituents.[20,21] The more common range

TABLE 4: Harmonic Theoretical and Scaled Vibrational Frequencies (cm^{-1}) of Silanol and Its Oligomers

monomer			dimer		trimer		tetramer		
unsc.[a]	sc.[b]	CCSD[c]	unsc.[a]	sc.[d]	unsc.[a]	sc.[d]	unsc.[a]	sc.[d]	assignment
3903	3750	3916	3880	3728	3564	3475	3392	3308	ν OH
			3671	3579	3563	3475	3347	3264	
					3488	3402	3347	3264	
							3235	3155	
2276	2228	2254	2289	2240	2263	2215	2261	2213	ν'_{as} SiH$_3$
			2259	2211	2262	2214	2261	2213	
					2262	2214	2261	2213	
							2261	2213	
2223	2176	2250	2243	2196	2231	2184	2236	2188	ν''_{as} SiH$_3$
			2240	2193	2229	2182	2234	2186	
					2229	2182	2234	2186	
							2233	2185	
2215	2168	2248	2208	2161	2226	2179	2231	2184	ν_s SiH$_3$
			2197	2150	2224	2177	2230	2182	
					2224	2177	2230	2182	
							2230	2182	
1011	988	1011	1023	992	1017	996	1018	997	δ_s SiH$_3$
			999	977	994	972	997	974	
					994	972	997	974	
							993	969	
981	963	974	984	953	984	955	978	954	δ_{as}' SiH$_3$
			969	945	965	945	975	952	
					965	945	975	952	
							972	950	
963	939	974	966	945	964	942	965	942	δ_{as}'' SiH$_3$
			960	939	962	941	965	942	
					962	941	965	941	
							965	941	
889	912	925	1008	1044	1272	1344	1352	1369	δ SiOH
			939	999	1061	1108	1188	1237	
					1061	1108	1188	1237	
							1117	1232	
830	854	858	880	898	889	906	885	901	ν SiO
			840	856	854	874	884	890	
					854	874	874	894	
							874	894	
723	720	725	751	750	749	750	733	730	ρ'' SiH$_3$
			728	727	733	736	733	730	
					733	736	729	729	
							726	723	
682	690	695	721	718	725	726	710	707	ρ' SiH$_3$
			718	716	725	726	707	706	
					708	729	707	706	
							698	703	
202	202	198	91	92	65	65	92	92	τ SiH$_3$
			76	77	65	65	80	78	
					59	59	76	75	
							76	75	
Intermolecular Vibrations									
			614	620	785	785	828	845	δ H···O−H
					570	570	811	818	(out-of-plane)
					570	570	811	818	
							800	823	
			253	253	143	143	146	146	δ H···O−H
					51	65	65	65	(in-plane)
					51	65	65	65	
							63	63	
			169	169	194	194	268	268	ν O−O
					194	194	242	242	
					179	179	242	242	
							152	152	
			46	47	22	22	57	57	τ H−O···H−O
							54	54	
			37	37	13	13	43	43	τ H−O···H−O
							43	43	
			27	27	11	11	28	28	τ H−O···H−O
							10	10	

[a] B3LYP/DZP+diff; this work. [b] Scale factors for the siloxy group refined for CH$_3$OSiH$_3$ with the fixed scale factors of the methoxy group. They are $c_{SiH} = 0.958$, $c_{SiO} = 1.046$ $c_{SiH3def} = 0.952$, and $c_{SiH3rock} = 0.988$. Scale factor for OH stretch ($c_{OH} = 0.923$) transferred from methanol. That for OH bend ($c_{SiOH} = 1.115$) refined to fit the observed frequencies 859 (SiH$_3$OH), 874 (SiD$_3$OD), 851 (SiH$_3$^{18}OH), and 850 cm^{-1} (SiD$_3$^{18}OD).[113] [c] Reference 10. [d] Scale factors for oligomers are transferred from the monomer with the exclusion of $c_{OH} = 0.951$ for H-bonded OH, which is transferred from the water dimer.

TABLE 5: Predicted Frequencies,[a] in cm^{-1}, and IR Intensities, in km mol^{-1}, (in Parentheses) of the OH Stretching Vibrations of Methanol and Silanol Clusters. For Methanol Clusters They Are Compared with Experimental Data

dimer		trimer		tetramer		
theor.	exp.[b]	theor.	exp.[c]	theor.	exp.[c]	exp.[d]
			Methanol			
3694 (42)	3684	3498 (871)	3503	3344 (12)	3335	
3584 (544)	3574	3485 (926)	3472	3302 (2091)	3270	3293
		3424 (35)	3433	3302 (2091)		
				3199 (0)		
			Silanol			
3728 (102)		3475 (1455)		3308 (388)		
3580 (862)		3475 (1455)		3264 (2874)		
		3402 (0)		3264 (2874)		
				3155 (0)		

[a] The B3LYP/DZP+diff force field scaled with the factor of the H-bonded OH stretch (0.951) transferred from the water dimer; in methanol and silanol dimers, the scale factor 0.923 for free OH sretching coordinates is taken from the methanol monomer. [b] Reference 91. [c] Reference 92. [d] Reference 114.

for these purposes is that of OH stretching vibrations. There are no experimental data on silanol, but certain bands of methanol clusters in this region were ascribed to dimers,[91] trimers,[92] and tetramers.[85,114] The general agreement of our predicted (with fixed scaling factors) vibrational frequencies of methanol clusters with the experiment is fair (Table 5), although in the methanol trimer the predicted separation between the two high-frequency bands (13 cm^{-1}) is considerably smaller than the experimental one (31 cm^{-1}). Likewise, the calculated IR intensities for the trimer also differ from the experimental ones: the predicted intensities of the two high frequency components are higher by 1 order of magnitude than that of the low frequency totally symmetric component, whereas in the experiment, the intensities of the high and low frequency bands are nearly equal.[92] Thus, the theoretical spectrum is closer to that of the C_{3h} symmetry group, under which two upper vibrations belong to the E irreducible representation (IR active), whereas the lower one belongs to A_1 (Raman active). Therefore, the B3LYP equilibrium geometry and force field of the methanol trimer underestimates the deviation of the structure from that of C_{3h}.

Because experimental OH stretching frequencies either for the isolated SiH_3OH molecule or for silanol clusters are not available, we cannot compare directly our predicted frequencies with the experiment. However, there exist spectral data on trimethylsilanol in different phases.[19−22] Although the structure of the trimethylsilanol liquid phase is unknown, we may consider that the OH stretching frequency of the tetramer is close to the hydrogen bond network limit. This assumption is based on the fact that the experimental frequency of the water tetramer 3416 cm^{-1} [68] is close to 3415 cm^{-1} for liquid water.[64] The experimental ν OH IR band in the gas phase of $(CH_3)_3SiOH$ is 3737 cm^{-1}.[21] Our predicted value for the silanol monomer is 3750 cm^{-1}. This is a good agreement with the gas-phase experimental frequency of $(CH_3)_3SiOH$, especially if one takes into account the fact that the methyl substitution in silanol results in the 7 cm^{-1} decrease of the νOH frequency. This estimate is based on the calculation of the vibrational spectrum of trimethylsilanol, details of which will be reported elsewhere. The experimental IR frequency in the liquid phase is 3290 cm^{-1}.[21] This value is within the range of our predicted frequencies of IR active vibrations for tetramer, i.e., 3308 and 3264 cm^{-1}.

Conclusions

1. Cyclic structures with S_4 symmetry, similar in the hydrogen-bond arrangement to that of the water tetramer, were found as minima at the PES of methanol and silanol tetramers.

2. The cyclic silanol trimer, in contrast to the water and methanol trimers, has a planar hydrogen-bond ring.

3. In the $(ROH)_n$ (R = H, CH_3, and SiH_3) systems the interatomic O−O separation and hence the hydrogen bond strength grow with n and in going from H to SiH_3.

4. The silanol tetramer is characterized by the largest binding energy among the systems studied in this work as well as by the highest binding enthalpy per monomer. This advantage of the tetramers may be the reason for the fact that the tetrameric arrangement of silanols is the most common pattern of the hydrogen bonding among the structures of silanols in the condensed phase determined by the X-ray diffraction.

5. Along with the red shift of the OH stretchings, the most notable tendency in the predicted vibrational frequency changes with the cluster size is the blue shift of ROH bendings (R = H, CH_3, and SiH_3). This shift in silanols is substantially higher than those for water and methanol (compare the 463 cm^{-1} increase in the silanol δ SiOH frequency in going from the monomer to tetramer to those of 116 cm^{-1} for the methanol δ COH frequency and 75 cm^{-1} for the water δ HOH frequency).

6. The predicted OH stretching frequencies for the methanol dimer and trimer (with the OH scale factor transferred from the water dimer) are in a good agreement with the experimental ones. Predicted frequencies of the IR active ν OH vibrations for silanol tetramer 3264 cm^{-1} (E) and 3308 cm^{-1} (A) are close to the observed IR value for liquid trimethylsilanol, i.e., 3290 cm^{-1}.

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