

## Structure and energetics of the hydrogen-bonded water and methanol clusters

J. Jaroniec<sup>1</sup>, K. Ziółkowska<sup>2</sup>, P. Borowski<sup>3</sup>, T. Janowski<sup>4</sup> and K. Woliński<sup>5</sup>  
*Wydział Chemii, Uniwersytet Marii Curie-Skłodowskiej  
Pl. M. C. Skłodowskiej 3, 20-031 Lublin, Poland*

The DFT/B3LYP/6-311G(d,p) study of water and methanol hydrogen bonded clusters is presented. The effect of hydrogen bond formation on the geometry of clusters is considered. With increasing cluster size shortening of the hydrogen bond as large as  $\approx 0.2 \text{ \AA}$  is observed. The accurate binding energies, corrected for the basis set superposition error, are reported. They reflect strong cooperative effects accompanying the hydrogen bond formation. The maximal value of binding energy per hydrogen bond is observed for cyclic hexamers. Comparison with earlier studies on water clusters is carried out. The obtained results are discussed in terms of the cluster populations in the bulk phase.

### 1. INTRODUCTION

The hydrogen bonded liquids, such as water, alcohols, etc., reveal specific spectroscopic and thermodynamical properties. They are commonly described in terms of the thermal equilibrium of hydrogen bonded molecular clusters of different sizes. For example, elongation of the O–H bond, accompanying the hydrogen bond formation, causes the red shift of the O–H bond stretch frequency, usually by more than  $100 \text{ cm}^{-1}$ . The upfield migration of the hydroxyl proton NMR signal in alcohols with temperature is attributed to breaking of the hydrogen bonds – small clusters with strongly shielded

<sup>1</sup> e-mail: [jaroniec@vsop406.umcs.lublin.pl](mailto:jaroniec@vsop406.umcs.lublin.pl), fax: (48-81)537-56-85, phone: (48-81)537-56-28

<sup>2</sup> e-mail: [ziolkowska@vsop405.umcs.lublin.pl](mailto:ziolkowska@vsop405.umcs.lublin.pl), fax: (48-81)533-33-48, phone: (48-81)537-56-14

<sup>3</sup> e-mail: [pibcio@vsop404.umcs.lublin.pl](mailto:pibcio@vsop404.umcs.lublin.pl), fax: (48-81)533-33-48, phone: (48-81)537-56-14

<sup>4</sup> e-mail: [janowski@vsop401.umcs.lublin.pl](mailto:janowski@vsop401.umcs.lublin.pl), fax: (48-81)537-56-85, phone: (48-81)537-56-28

<sup>5</sup> e-mail: [wolinski@vsop401.umcs.lublin.pl](mailto:wolinski@vsop401.umcs.lublin.pl), fax: (48-81)537-56-85, phone: (48-81)537-56-28

hydroxyl protons are favoured at high temperature. Also the enhanced association of molecules (monomers) at lower temperatures, causes the structure of a liquid to be more compact – the density of a liquid increases.

Proper description of physical features of hydrogen bonded liquids requires detailed knowledge of the properties of individual clusters. They can be computed with high accuracy with modern *ab initio* quantum mechanical programs. Water clusters were already subjected to theoretical investigations; a number of them were published over the last five years alone. For example, the structure and energetics of  $(\text{H}_2\text{O})_n$ ,  $n=12,16,20$  clusters was examined by molecular dynamics simulations [1]. Structure, energetics and IR spectra of medium-sized clusters,  $(\text{H}_2\text{O})_n$ ,  $n=7-10$ , were also computed [2-4]; the calculation included *ab initio* MP2 method in the determination of molecular geometry. The MP2 structures, binding energies and IR spectra of cage  $(\text{H}_2\text{O})_n$ ,  $n=11,12$  clusters were published recently [5]. The calculations were carried out with double zeta plus polarization basis set and included corrections for the basis set superposition error. Weinhold [6] considered a series of water clusters and reported their properties: electronic energies corrected for the basis set superposition error (BSSE), rotational and vibrational temperatures and zero point energy (ZPE) corrections. These data were used in a framework of the Quantum Cluster Equilibrium (QCE) theory [7] to compute the populations of clusters in liquid water as a function of temperature. Similar calculations were carried out for other hydrogen bonded systems, including N-methylacetamide [8], ethanol [9,10], etc. These authors were able to reproduce qualitatively a number of thermodynamical and spectroscopic features (including variation of the density, heat capacity, chemical shifts, quadrupole coupling constants, etc. with temperature). However, the low level of theory used to compute the clusters' properties (i.e. Self Consistent Field (SCF) method and small basis set) is one of the factors responsible for only qualitative agreement between experimental and theoretical data.

In this paper we present the detailed Density Functional Theory (DFT) [11] study of molecular clusters of water and methanol. Clusters  $(\text{H}_2\text{O})_n$ ,  $n=1,2,3,4,5,6,7,8,12$  and  $(\text{CH}_3\text{OH})_n$ ,  $n=1,2,3,4,5,6,7$  are considered. The limited set of clusters was chosen on account of their expected dominance in the liquid phase over the range of temperatures [6,9]. The calculations include: molecular geometry optimization, zero point energy corrections and basis set superposition error corrections. The average energy per hydrogen bond for all clusters are also reported and discussed in terms of the cooperativity of hydrogen bonding interactions. The presented results can be used in order to predict the composition of liquid water and methanol within the QCE model. We believe, that the determination of cluster populations from more accurate data will provide a new insight in the structure of the hydrogen bonded liquids.

It will be also helpful in the rigorous judgement on the predictive capabilities of the QCE model. We will address these problems in the forthcoming papers. In Section 2 the details of DFT calculations are reported. In Sections 3 and 4 the results for isolated monomers and clusters are described and discussed. In Section 5 we state our conclusions.

## 2. COMPUTATIONAL PROCEDURE

It is well known that the simplest *ab initio* method – the SCF method – often fails to predict accurately the equilibrium geometry of molecules in near-degenerate ground states. On the other hand reliable geometries for typical closed-shell systems can be obtained already at the SCF level of theory, provided the relevant basis set is chosen. In our previous paper [12] we investigated ethanol molecule – the well-behaved, closed-shell system. However, the geometry of the C–O–H fragment turned out to be somewhat inaccurate at the SCF level. Correlated *ab initio* methods (e.g. MCSCF, MP2, etc.) are usually superior to SCF calculations. Accurate molecular conformations are also predicted by the Density Functional Theory [13], in particular when the B3LYP exchange–correlation potential [11,14,15] is used. For the ethanol molecule [12] – the system similar to those considered here – the method reproduces well the experimental (microwave) data. In this paper molecular geometries were optimized at the DFT/B3LYP level using the 6-311G(d,p) basis set [16] for all water and methanol clusters. The zero point energy corrections were computed within the harmonic approximation by the standard FG–matrix method [17] for all clusters at the same level of theory.

The binding energies of the  $M_n$  clusters ( $M = \text{H}_2\text{O}, \text{CH}_3\text{OH}$ ),

$$\Delta E_n = nE_{\text{mon}} - E_n \quad (1)$$

were corrected for the well known basis set superposition error (overestimating binding energies in small basis sets), using counterpoise (CP) correction method [18]: the energy of each monomer  $\mu$  in the cluster  $M_n$  is computed

(i) using the basis set of the whole cluster –  $E_{n\mu}^{(\text{bas})}$ , and (ii) using the basis set of the monomer alone –  $E_{n\mu}^{(\text{ref})}$ . The CP correction, defined as

$$\delta_n^{\text{CP}} = \sum_{\mu=1}^n (E_{n\mu}^{(\text{ref})} - E_{n\mu}^{(\text{bas})}) \quad (2)$$

is positive and includes the effect of a small distortion of a monomer in the cluster. The counterpoise corrected binding energy is thus given by the following formula:

$$\Delta E_n^{\text{CP}} = \Delta E_n - \delta_n^{\text{CP}} \quad (3)$$

The percentage cooperative enhancement (relative to dimer) was computed as

$$(\% \text{ coop})_n = \frac{\frac{\Delta E_n^{\text{CP}}}{m_n} - \Delta E_{\text{dimer}}^{\text{CP}}}{\Delta E_{\text{dimer}}^{\text{CP}}} \quad (4)$$

where  $m_n$  denotes the number of the hydrogen bonds in the cluster.

All calculations reported in this paper were performed with the parallel version of the *ab initio* quantum chemistry PQS package [19,20] implemented for a cluster of Pentium II/400 MHz PC machines. The maximum speedup obtained with 12 CPUs was about 11 as compared to the single processor run.

### 3. THE WATER AND METHANOL MONOMERS

In Tab. 1 theoretical and experimental equilibrium geometries of water and methanol molecules are compared. Bond lengths and valence angles predicted by the DFT/B3LYP/6-311G(d,p) method are very close to the microwave spectroscopy data. The relative error usually amounts to less than 1%, indicating high accuracy of the reported values. It should be emphasized, that the molecular geometry (as well as other properties: rotational and vibrational temperatures, etc.) used in the QCE modeling of liquid water structure by Weinhold [6], were obtained at much lower level of theory (i.e. SCF/3-21G). Consequently, the bond lengths were too short (rotational temperatures inaccurate) and vibrational frequencies (and temperatures) too high. We may also expect substantial errors in Weinhold's binding energies of hydrogen bonded clusters. As we shall see they are overstabilized at this level by as much as 20–30%. It is clear, that the determination of reliable cluster populations should be based on much more accurate than SCF/3-21G data.

Tab. 1. Theoretical and experimental geometries of water and methanol molecules

| Molecule |                           | Bond lengths (in Å) |       |       | Valence angles (in °) |        |
|----------|---------------------------|---------------------|-------|-------|-----------------------|--------|
| Water    | Theory Expt. <sup>a</sup> | O–H                 |       |       | H–O–H                 |        |
|          |                           | 0.962               |       |       | 103.82                |        |
|          |                           | 0.9575              |       |       | 104.51                |        |
| Methanol | Theory Expt. <sup>a</sup> | C–O                 | C–H   | O–H   | C–O–H                 | H–C–H  |
|          |                           | 1.421               | 1.096 | 0.961 | 107.84                | 108.27 |
|          |                           | 1.425               | 1.094 | 0.945 | 108.53                | 108.63 |

<sup>a</sup>See eg. [24]

#### 4. THE WATER AND METHANOL CLUSTERS

The *ab initio* based QCE calculations of populations in liquid water [7] included 9 water clusters, the largest of which was octamer. This model was extended: 18-cluster QCE treatment [21] comprised ring, tetrahedral and fullerene-like clusters up to 26-mers. Nevertheless all the calculations of clusters' properties were carried out at the simple SCF/3-21G level of theory. For this reason only qualitative significance should be given to the predicted populations of water clusters in the bulk phase.

In this paper we report results of a series of DFT/B3LYP calculations on water clusters (up to 12-mers) and methanol clusters (up to 7-mers). Geometry optimization and harmonic vibrational frequencies calculations (at the optimized geometries) were carried out at the DFT/B3LYP/6-311G(d,p) level. All frequencies turned out to be real indicating that considered structures are stable (they correspond to local minima at the potential energy surface). Energetics, including ZPE and BSSE corrections, and the most important geometrical parameters are presented in Tables 2 and 3. The structures are shown in Figures 1 and 2.

Geometry optimization usually led to the cyclic clusters. Only in the case of water and methanol dimers, linear structure is more stable than the corresponding cyclic structure; the latter is in fact transition state due to high strain in the four-membered ring. Only one linear cluster – the methanol pentamer – was found to be stable. However, its total binding energy, Eq. (1), is by about 9 kcal/mol higher than for the cyclic counterpart. It is hard to judge at this point whether the global minima on the potential energy surfaces were found. It should be emphasized that the geometry optimization of hydrogen bonded species is a difficult task due to the presence of numerous local minima and transition states. Our experience with similar calculations on ethanol clusters [12] leads to the conclusion that local minima of cyclic structures for a given number of monomers in the cluster are very close in energy. In fact they have the same topology: the oxygen-hydrogen ring is preserved and the only geometrical differences are in the relative orientation of the hydrofobic C–C chains. As discussed elsewhere [7] it is sufficient to include only one representative  $n$ -mer in the QCE calculations. This is why we did not carry out a search for global minima of water and methanol clusters.

In all water and methanol clusters the lengths of the free OH bonds ( $r_{\text{OH}}^{(0)}$ ; refer to Figures 1b' and 2b' for details), i.e. bonds that do not participate in hydrogen bonding, remain essentially the same as they were in corresponding monomers ( $\approx 0.96 \text{ \AA}$ ).

Table 2. The water clusters: DFT/B3LYP/6-311G(d,p) (energies in kcal/mol<sup>a</sup>, bond lengths in Å<sup>b</sup>)

| Structure | $m_n^c$ | $\Delta E_n$ | $\frac{\Delta E_n}{m_n}$ | $\delta_n^{CP}$ | $\Delta E_n^{CP}$ | $\frac{\Delta E_n^{CP}}{m_n}$ | % coop <sup>d</sup> | ZPE     | $r_{OH}^{(f)}$ | $r_{OH}$ | $r_{OH}^{(h)}$ |
|-----------|---------|--------------|--------------------------|-----------------|-------------------|-------------------------------|---------------------|---------|----------------|----------|----------------|
| Monomer   | 0       |              |                          |                 |                   |                               |                     |         |                |          |                |
| Dimer     | 1       | 7.637        | 7.637                    | 2.871           | 4.766             | 4.766                         | 0.0                 | 13.380  | 0.9620         | 0.970    | 1.920          |
| Trimer-1  | 3       | 23.276       | 7.759                    | 8.582           | 14.694            | 4.898                         | 2.8                 | 28.979  | 0.963          | 0.978    | 1.873          |
| Trimer-2  | 3       | 24.600       | 8.200                    | 8.681           | 15.920            | 5.307                         | 11.4                | 46.284  | 0.961          | 0.979    | 1.860          |
| Tetramer  | 4       | 41.178       | 10.294                   | 13.075          | 28.102            | 7.026                         | 47.4                | 46.426  | 0.962          | 0.986    | 1.743          |
| Pentamer  | 5       | 53.344       | 10.669                   | 16.127          | 37.217            | 7.443                         | 56.2                | 62.568  | 0.961          | 0.988    | 1.710          |
| Hexamer   | 6       | 65.318       | 10.886                   | 17.851          | 47.467            | 7.911                         | 66.0                | 78.175  | 0.961          | 0.988    | 1.698          |
| Heptamer  | 7       | 80.871       | 11.553                   | 27.375          | 53.496            | 7.642                         | 60.3                | 93.809  | 0.964          | 0.985    | 1.760          |
| Octamer   | 12      | 109.664      | 9.139                    | 37.363          | 72.301            | 6.025                         | 26.4                | 111.051 | 0.961          | 0.999*   | 1.664*         |
|           |         |              |                          |                 |                   |                               |                     | 129.427 |                | 0.976*   | 1.871*         |
|           |         |              |                          |                 |                   |                               |                     |         |                | 0.976†   | 1.871†         |
| Dodecamer | 18      | 170.612      | 9.478                    | 55.318          | 115.295           | 6.405                         | 34.4                | 194.206 | 0.962          | 1.001*   | 1.635*         |
|           |         |              |                          |                 |                   |                               |                     |         |                | 0.977*   | 1.815*         |
|           |         |              |                          |                 |                   |                               |                     |         |                | 0.975†   | 1.875†         |

<sup>a</sup>  $\Delta E_n$  – binding energy, Eq. (1),  $\delta_n^{CP}$  – basis set superposition error, Eq. (2),  $\Delta E_n^{CP} = \Delta E_n - \delta_n^{CP}$ , ZPE – zero point energy correction.

<sup>b</sup>  $r_{OH}^{(f)}$  – length of a free OH bond,  $r_{OH}^{(h)}$  and  $r_{OH}$  – lengths of a pair of hydrogen bond and OH bond in the O...H–O fragments (Figure 1 b'); average bond lengths are reported.

<sup>c</sup> Number of hydrogen bonds in the cluster.

<sup>d</sup> Eq. (4).

\* Average bond lengths in the planes of tetramers/hexamers (Figure 1 i').

† Average bond lengths between the planes of tetramers/hexamers (Figure 1 i').

Table 3. The methanol clusters: DFT/B3LYP/6-311G(d,p) (energies in kcal/mol<sup>a</sup>, bond lengths in Å<sup>b</sup>)

| Structure  | $m_n^c$ | $\Delta E_n$ | $\frac{\Delta E_n}{m_n}$ | $\delta_n^{CP}$ | $\Delta E_n^{CP}$ | $\frac{\Delta E_n^{CP}}{m_n}$ | % coop <sup>d</sup> | ZPE     | $r_{OH}^{(f)}$ | $r_{OH}^{(h)}$ | $r_{CH}$ | $r_{CO}$ |
|------------|---------|--------------|--------------------------|-----------------|-------------------|-------------------------------|---------------------|---------|----------------|----------------|----------|----------|
| Monomer    | 0       | 7.716        | 7.716                    |                 |                   |                               |                     |         |                |                |          |          |
| Dimer      | 1       | 22.954       | 7.651                    | 3.142           | 4.574             | 4.574                         | 0.0                 | 32.095  | 0.961          | 0.969          | 1.096    | 1.421    |
| Trimer     | 3       | 38.342       | 9.585                    | 7.530           | 15.423            | 5.141                         | 12.4                | 100.120 | 0.961          | 0.977          | 1.096    | 1.423    |
| Tetramer   | 4       | 41.390       | 10.348                   | 11.119          | 27.222            | 6.806                         | 48.8                | 133.816 |                | 0.985          | 1.095    | 1.423    |
| Pentamer-1 | 4       | 50.335       | 10.067                   | 13.741          | 27.649            | 6.912                         | 51.1                | 167.091 | 0.961          | 0.983          | 1.095    | 1.427    |
| Pentamer-2 | 5       | 61.819       | 10.303                   | 14.679          | 35.657            | 7.131                         | 55.9                | 167.646 |                | 0.986          | 1.095    | 1.422    |
| Hexamer-1  | 6       | 62.346       | 10.391                   | 18.556          | 43.263            | 7.210                         | 57.6                | 201.548 |                | 0.986          | 1.095    | 1.423    |
| Hexamer-2  | 6       | 72.052       | 10.293                   | 17.883          | 44.463            | 7.411                         | 62.0                | 201.286 |                | 0.987          | 1.095    | 1.422    |
| Heptamer   | 7       |              |                          | 20.336          | 51.716            | 7.388                         | 61.5                | 234.689 |                | 0.987          | 1.095    | 1.421    |

<sup>a</sup> $\Delta E_n$  – binding energy, Eq. (1),  $\delta_n^{CP}$  – basis set superposition error, Eq. (2),  $\Delta E_n^{CP} = \Delta E_n - \delta_n^{CP}$ , ZPE – zero point energy correction.

<sup>b</sup> $r_{OH}^{(f)}$  – length of a free OH bond,  $r_{OH}^{(h)}$  and  $r_{OH}$  – lengths of a pair of hydrogen bond and OH bond in the O...H–O fragments (Figure 2 b'),  $r_{CH}$  and  $r_{CO}$  – lengths of CH and CO bonds; average bond lengths are reported.

<sup>c</sup>Number of hydrogen bonds in the cluster.

<sup>d</sup>Eq. (4).

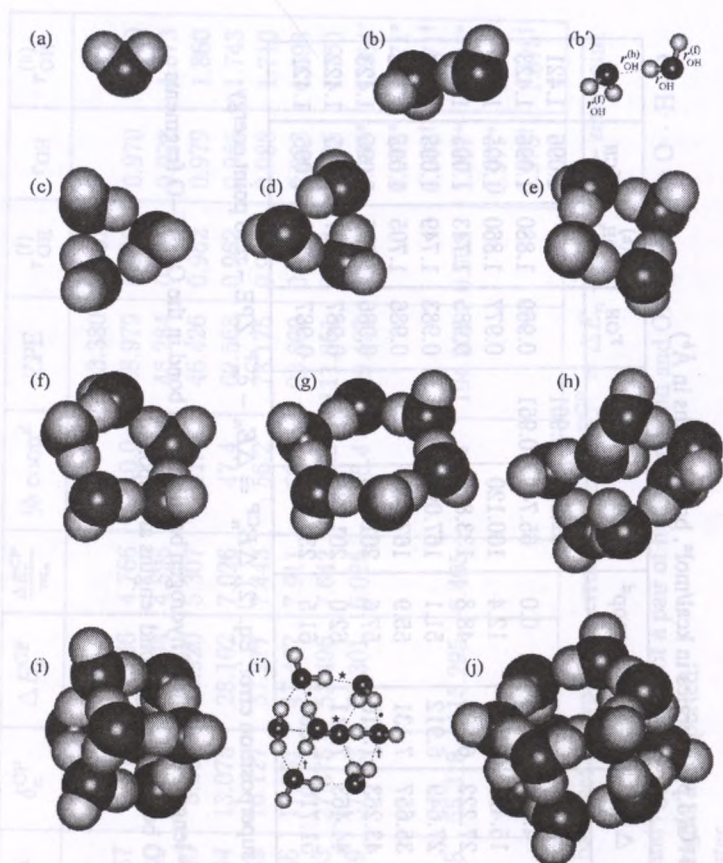


Fig. 1. Structures of water clusters: (a) monomer, (b) and (b') dimer, (c) trimer-1, (d) trimer-2, (e) tetramer, (f) pentamer, (g) hexamer, (heptamer, (i) and (i') octamer, (j) dodecamer

Also the CO and CH bond lengths ( $r_{CO}$  and  $r_{CH}$ ) in methanol do not vary with cluster size: they are equal to  $\approx 1.42$  Å and  $\approx 1.095$  Å respectively. The association of monomers to form larger clusters results in profound changes in the geometry of O $\cdots$ H–O fragments. With increasing cluster size the length of a hydrogen bond ( $r_{OH}^{(h)}$ ) decreases – from  $\approx 1.92$  Å (dimer) to  $\approx 1.70$  Å (higher cyclic clusters) for water and from  $\approx 1.88$  Å (dimer) to  $\approx 1.69$  Å (heptamer) for methanol. This shortening of a hydrogen bond by about  $\approx 0.2$  Å is accompanied by elongation (by about  $\approx 0.02$  Å) of the OH bond in the O $\cdots$ H–O fragment. It should be noted, that incorporation of a large number of water molecules in the cluster results in spatial rather than planar structures (see eg. Figures 1i' and 1j), containing hydrogen bonds of different lengths. Indeed, the iterative geometry optimization of water octamer, with initial



geometry of cyclic type, led to the cubic structure shown in Figure 1 (i). Note in passing, that cyclic octamer was incorrectly predicted to be stable at the SCF/3-21G level of theory [6]. The described structural trends are characteristic to all hydrogen bonded systems [6,9,12].

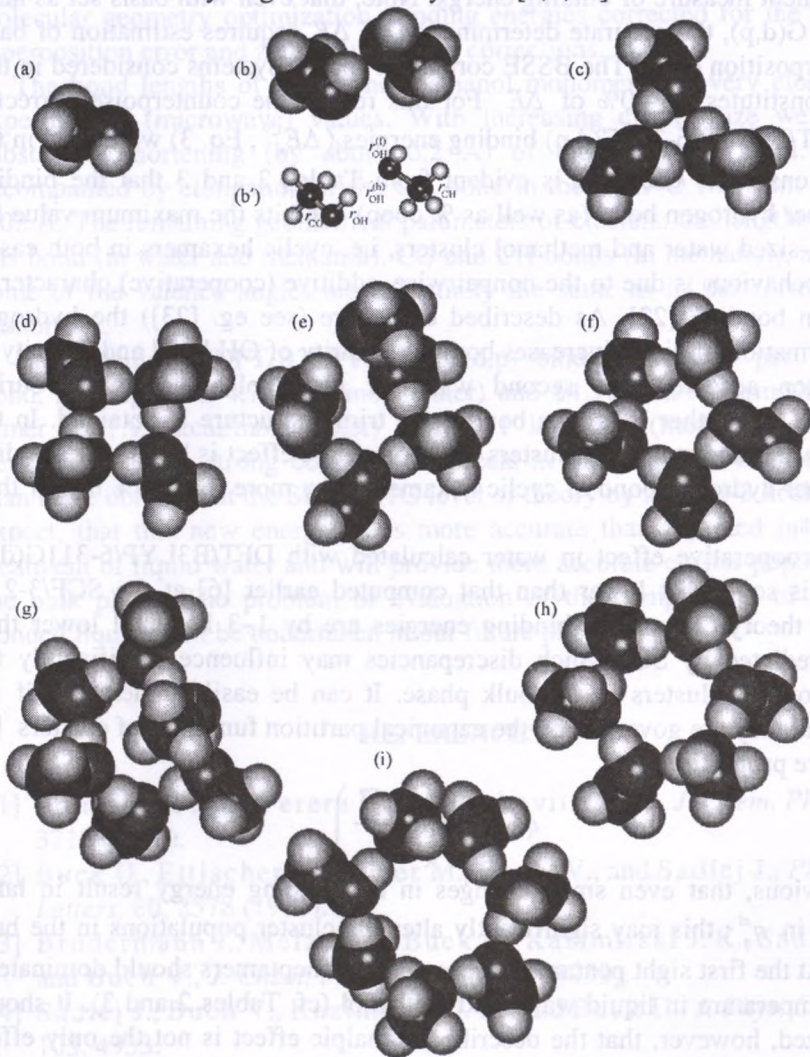


Fig. 2. Structures of methanol clusters: (a) monomer, (b) and (b') dimer, (c) trimer, (d) tetramer, (e) pentamer-1, (f) pentamer-2, (g) hexamer-1, (h) hexamer-2, (i) heptamer

The content of a particular cluster in the bulk phase is closely related to its binding energy ( $\Delta E$ ) per hydrogen bond, i.e.  $\Delta E/m_n$ . The so-called percentage cooperative enhancement relative to dimer (% coop, Eq. 4), is a convenient measure of binding energy. Note, that even with basis set as large as 6-311G(d,p), the accurate determination of  $\Delta E$  requires estimation of basis set superposition error. The BSSE correction for the systems considered in this paper constitutes 30–40% of  $\Delta E$ . For this reason the counterpoise corrected [18] DFT/B3LYP/6-311G(d,p) binding energies ( $\Delta E_n^{\text{CP}}$ , Eq. 3) were used in the calculations of % coop. It is evident from Tables 2 and 3 that the binding energy per hydrogen bond (as well as % coop) exhibits the maximum value for medium-sized water and methanol clusters, i.e. cyclic hexamers in both cases. Such a behaviour is due to the nonpairwise-additive (cooperative) character of hydrogen bonding [22]. As described elsewhere (see eg. [23]) the hydrogen bond formation in dimer increases both the polarity of OH bond and basicity of the proton acceptor (the second water or methanol molecule) favouring formation of another hydrogen bond – the trimer structure is obtained. In the case of water and methanol clusters the cooperative effect is large – the binding energy per hydrogen bond of cyclic hexamers is by more than 60% higher than in dimers.

The cooperative effect in water calculated with DFT/B3LYP/6-311G(d,p) method is somewhat lower than that computed earlier [6] at the SCF/3-21G level of theory. Also DFT binding energies are by 1–3 kcal/mol lower than those predicted by SCF. Such discrepancies may influence significantly the populations of clusters in the bulk phase. It can be easily understood if we recall that they are governed by the canonical partition functions of clusters [7] which are proportional to

$$q_n^{\text{cl}} = \exp\left(\frac{\Delta E_n^{\text{CP}}}{kT}\right)$$

It is obvious, that even small changes in the binding energy result in large changes in  $q_n^{\text{cl}}$ ; this may significantly alter the cluster populations in the bulk phase. At the first sight pentamers, hexamers and heptamers should dominate at room temperature in liquid water and methanol (cf. Tables 2 and 3). It should be realized, however, that the described enthalpic effect is not the only effect responsible for the composition of hydrogen bonded liquids [6,7]. Numerous accessible rotational states and low energy vibrational states enlarge the entropy of a system. This may efficiently exclude some of the clusters in favour of others. The rigorous treatment of both enthalpic and entropic effects is provided by the QCE theory [7]. Implementation of QCE code is one of our main goals in the nearest future.

## 5. CONCLUSIONS

We calculated a number of properties of the water and methanol clusters using the DFT/B3LYP/6-311G(d,p) approach. The calculations included: molecular geometry optimization, binding energies corrected for the basis set superposition error and zero point energy corrections.

The bond lengths of water and methanol monomers are very close to the experimental (microwave) values. With increasing cluster size we observe substantial shortening (by about 0.2 Å) of the hydrogen bond. This is accompanied by elongation of the OH bond in the O<sup>⋯</sup>H-O fragment by about 0.02 Å. The remaining geometrical parameters of clusters: the lengths of a free OH bond (in water and methanol), CO and CH bonds (in methanol), as well as some of the valence angles are essentially the same as in the corresponding monomers.

The calculated DFT/B3LYP/6-311G(d,p) binding energies per hydrogen bond, ranging from 4.77 kcal/mol (water) and 4.57 kcal/mol (methanol) for dimer to 7.91 kcal/mol (water) and 7.41 kcal/mol (methanol) for cyclic hexamer, indicate strong cooperative effects in both liquids. They are lower than these obtained at the SCF/3-21G level of theory by about 1-3 kcal/mol. We expect, that this new energetics is more accurate than reported in the QCE treatment of liquid water and will provide more accurate cluster populations in the bulk phase. The problem of evaluation of the composition of hydrogen bonded liquids will be undertaken in our future papers.

## REFERENCES

- [1] Sremaniak L. S., Perera L., and Berkovitz M. L., *J. Chem. Phys.*, 105, 3715 (1996).
- [2] Buck U., Ettischer I., Melzer M., Buch, V., and Sadlej J., *Phys. Rev. Letters*, 80, 2578 (1998).
- [3] Bruderemann J., Melzer M., Buck U., Kazimirski J. K., Sadlej J., and Buch V., *J. Chem. Phys.*, 110, 10649 (1999).
- [4] Sadlej J., Buch V., Kazimirski J. K., and Buck U., *J. Phys. Chem. A*, 103, 4933.
- [5] Sadlej J., *Chem. Phys. Letters*, 333, 485 (1999).
- [6] Weinhold F., *J. Chem. Phys.*, 109, 373 (1998).
- [7] Weinhold F., *J. Chem. Phys.*, 109, 367 (1998).
- [8] Ludwig R., Reis O., Winter R., Weinhold F., and Farrar T. C., *J. Phys. Chem. B*, 102, 9312, 7 (1998)
- [9] Ludwig R., Weinhold F., and Farrar T. C., *Mol. Phys.*, 97, 465 (1999).

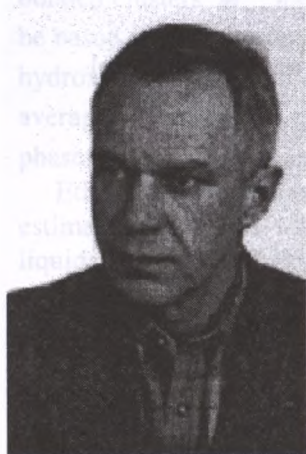
- [10] Ludwig R., Weinhold F., and Farrar T. C., *Mol. Phys.*, 97, 479 (1999).
- [11] Parr R. G., and Yang W., *Density-Functional Theory of Atoms and Molecules*. Oxford University Press, New York, 1989.
- [12] Borowski P., Janowski T., and Woliński K., *Mol. Phys.*, 98, 1331 (2000).
- [13] Schemer A. C., Baker J., and Andzelm J., *J. Comput. Chem.*, 18, 775 (1997).
- [14] Becke A. D., *J. Chem. Phys.*, 98, 5648 (1993).
- [15] Lee C., Yang W., and Parr R. G., *Phys. Rev. B*, 37, 785 (1993).
- [16] Krishnan R., Binkley J. S., Seeger R., and Pople J. A., *J. Chem. Phys.*, 72, 650 (1980).
- [17] Wilson E. B., Jr, Decius J. C., and Cross P. C., *Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra*. Dover Publications, Inc., New York, 1955.
- [18] Boys S. F., and Bernardi F., *Mol. Phys.*, 19, 553 (1970).
- [19] Woliński K., Haacke R., Hinton J. F., and Pulay P., *J. Comput. Chem.*, 18, 816 (1997).
- [20] PQS version 2.2, *Parallel Quantum Solutions*, 2013 Green Acres Road, Fayetteville, Arkansas 72703.
- [21] Ludwig R., and Weinhold F., *Phys. Chem. Chem. Phys.*, 2, 1613 (2000).
- [22] Frank H. S., *Acc. Chem. Res.*, 29, 441 (1957).
- [23] Buckingham A. D., in *Theoretical Treatments of Hydrogen Bonding*. ed. D. Hadzi. John Wiley & Sons, Ltd., Chichester, 1997 (p. 1).
- [24] D. R. Lide, ed. *CRC Handbook of Chemistry and Physics: 1913-1995*. CRC Press, Inc., Boca Raton, 1995.

## CURRICULA VITAE



**Piotr Borowski** was born in Lublin (Poland) in 1966. Studies of chemistry in the Faculty of Chemistry, Maria Curie-Skłodowska University in Lublin, Poland in 1984-1989. Scholarship awarded by the Minister for National Education in 1988. The prize awarded by the Minister for Labour and Social Policy for the achievements during the studies in 1989. Received Master's degree in 1989 (supervisor: Professor Andrzej Patrykiewicz). Employed as an assistant in the Department of Chemical Physics, Maria Curie-Skłodowska

University in 1989. Ph.D. student in the Department of Theoretical Chemistry, University of Lund, Sweden in 1990-1995 (supervisor: Professor Bjorn O. Roos). Associated Western Universities Postdoctoral Fellow in the Pacific Northwest Laboratory and University of Pittsburgh (USA) in 1995-1996 (advisors: Professor Jeffrey A. Nichols and Professor Kenneth D. Jordan). Main fields of interest: applied quantum chemistry, theoretical description of the NMR spectra of hydrogen bonded liquids, theoretical studies of molecular vibrations. The author of a textbook on molecular spectroscopy *Wybrane zagadnienia spektroskopii molekularnej (Selected Problems of Molecular Spectroscopy)* (2001). Published 15 original papers.



**Krzysztof Woliński** was born in Poland in 1951. Graduated from University of Maria Curie-Skłodowska (UMCS Lublin) in 1974. Received his Ph.D. in 1981 and habilitation in 1995. Since 1995 employed as an associate professor in the Department of Theoretical Chemistry of UMCS. Main interest in quantum chemistry: perturbation theory, magnetic properties, parallel computing.

He has wide scientific collaborations with leading quantum chemistry groups in world. In 1985-1988 he worked with prof. B. Roos at the University of Lund (Sweden). Since 1986 until now he collaborates closely with prof. Peter Pulay from the University of Arkansas (USA) where he spent all together over nine years. In 1994 he was appointed by the very prestigious Pacific Northwest National Laboratory in Richland (USA), one of the nine federal laboratories in United States.