

Theoretical study on icosahedral water clusters

Oleksandr Loboda* and Vladyslav Goncharuk

*A.V. Dumansky Institute of Colloid Chemistry and Chemistry of Water,
National Academy of Sciences of Ukraine,
42 Vernadskogo av., Kyiv 03142, Ukraine*

Abstract

The authors present structural study of different gas hydrates by using DFT hybrid method. A new concept of viewing icosahedral cluster as expansion of dodecahedral subvolumes is introduced. The investigated structures exhibit up to 280 water molecules. Structural and orientational features of various guest molecules occupied the central volume of clusters are established. It was found that monomer of water has the highest stabilization energy in studied clusters. The conformational changes in dimer and trimer water molecules upon incorporation into hydrate cavity are discussed. The influence of second and third order solvent shells is illustrated on example of icosahedral water cluster derivatives.

Keywords: DFT, icosahedral clusters.

* Corresponding author.

E-mail address: o.a.loboda@icwc.kiev.ua (O. Loboda).

I. INTRODUCTION

It is well known that gas hydrates exist in the form of polyhedral water clusters hosting different small gas molecules¹. The polyhedral water clusters can be classified in 12, 14 or 16-hedral units. The simplest dodecahedral water cluster is composed of 20 water molecules, which make ensemble of 12 pentamers. Depending on the orientation of non-bonding hydrogens one can obtain different types of dodecahedral water clusters². For example, the application of graph theoretical techniques to the dodecahedral network of $(\text{H}_2\text{O})_{20}$ produces more than 30000 isomers³.

In our paper the main focus will be on dodecahedral water cluster (5^{12}) in which non-bonding hydrogens belong to the two pentagons, which are opposite to each other (Figure 1a). This highly symmetric (S_{10}) spherical cage has been already used as model for interactions between atmospheric radicals and cloud droplets⁴.

It is important to note that the structure of $(\text{H}_2\text{O})_{20}$ has been the subject of numerous discussions^{2,5,6} due to the absence of experimental information. So far among variety of possible structural isomers theoreticians distinguish four major families of $(\text{H}_2\text{O})_{20}$ cluster: dodecahedron, fused cubes, face-sharing and edge sharing pentagonal prisms. The latter was found to be the most energetically stable^{2,7}. However our interest in dodecahedron constitutes from the ability of such type of clusters to be a good model for inclusion of guest molecules. Furthermore they may be used as building blocks of type I ice clathrates⁸. In this respect another important issue arises: transition from the threefold to the compact fourfold coordinated structural organisation. We believe that our study will contribute to the better understanding of the nature of that transition.

The above mentioned 5^{12} water cluster is the central part of the large icosahedral clusters studied here (Figure 1b,c). The model of icosahedral water cluster containing 280 water molecules was introduced in Ref.⁹. The proposed model gives reasonable explanation for many of anomalous properties of water such as pressure, viscosity, temperature and density behavior. In particular, the temperature-density relations can be explained in terms of reorganization of icosahedral cluster in two structural forms (collapsed and expanded) without breaking of hydrogen bonds. At low temperature the amount of expanded form of water cluster prevails which contributes to low density of water. As the temperatures increases

the transition in to less ordered collapsed structure i.e. more dense form facilitates due to the entropy and enthalpy considerations. The density (0.94 g cm^{-3}) of expanded form of icosahedral clusters studied here (Figure 1b,c) can be compared with the density (0.94 g cm^{-3}) of supercooled water at -45°C or with the the density of water (0.96 g cm^{-3}) which found around macromolecules^{9,12}. The dodecahedral water clusters are stable structures due to the balanced number of acceptor and donor pairs (2 donors, 2 acceptors). Though the proposed cluster has tetrahedral orientation, the formation of crystal structure is prevented by fivefold symmetry. This fact can be attributed to the effect of supercooled water.

The previous treatment of icosahedral cluster has been done by force -field methods without explicit impose of hydrogens and without guest molecules⁹. It was suggested that to the stability of low-density form of icosahedral cluster contribute solute molecules entrapped inside of cavities of cluster. In this paper we investigate by means of density functional theory the energetic outcome of hosting CO_2 and methane molecules in water derivatives of dodecahedral cluster. We also study the case of unbound free water and small water clusters as the guest molecules.

The choice of guest molecules is based on natural abundance of the CO_2 and CO_4 species in water environment. The carbon dioxide linked to global warming is accumulating by ocean. With the increased level of CO_2 , the pH of the water decreases, becoming more acidic and evidently toxic for living organisms. Therefore it is important to know how the CO_2 capture occurs in water solution.

The methane-centered cages attract a lot of interest due to the probable conversion of CH_4 hydrate into CO_2 hydrate, which may be thought as important source of hydrocarbon fuel¹⁰. Recently the methane-water clusters were examined under pressure¹¹. Though the clathrate cages around the guest methane molecule have been found less favorable than the nestlike structures, they did become low-energy local minima at high pressures. In this paper we try to address the following question: what are the energetical and structural changes take place upon expanding water network from simple dodecahedron into higher order solvent shells and to which extend it affects the guest molecules.

II. METHOD OF CALCULATIONS

Geometry optimizations were performed using the semiempirical PM3 Hamiltonian^{13,14} method as it is implemented in GAMESS program¹⁵. The single point energy calculations were done subsequently using B3LYP/3-21G method. The number of basis functions in our largest B3LYP calculation of $(\text{H}_2\text{O})_3@(\text{H}_2\text{O})_{280}$ were 3679 which is in upper limit of DFT capability. The stabilization energy SE is calculated as following: $\text{SE} = \text{E}[\text{M}@(\text{H}_2\text{O})_N] - \text{E}[\text{M}] - \text{E}[(\text{H}_2\text{O})_N]$, where M is the guest molecule, N is the number of water molecules (20,100,280). The stabilization energy per water molecule is defined: $\text{SEP} = \text{SE}/N$.

In order to avoid large errors in our calculated values the zero-point energy corrections and basis set superposition errors are not considered in the present study due to the reasons explained in details in Ref.¹⁶.

III. RESULTS AND DISCUSSION

The choice of studied molecules is shown on Fig 1. The elementary dodecahedral cage (Figure 1a) can be viewed as a four-level structure, where the top and bottom levels are represented by cyclic pentamer rings. Each of these ring constituent water molecule has one hydrogen participating in hydrogen bonding within the ring while the other hydrogen is 'free' dangling. The each of two middle levels also consist of five water molecules. However all hydrogens of this inner levels are not free and make hydrogen bonds within the adjacent pair of water molecules, having one hydrogen bond to connect two middle levels and the other hydrogen bond to connect bottom or top level. In this way 10 pentamers are formed on the side of the cluster. As we mentioned above only bottom and top levels have 'free' dangling OH bonds, thus the $(\text{H}_2\text{O})_{20}$ cluster in total possesses 30 hydrogen bonds and consists of 12 pentamer cyclic rings.

The stabilization energy values relative to separated H_2O molecules and SE per H_2O are tabulated in Table I. The cooperativity effect of water has almost linear tendency in respect to the number of water molecules involved in cluster formation. Thus the 1:5:14 ratio in number of water molecules relates to the 1:6:18 ratio in corresponding stabilization energies.

Table II has the results from inclusion of guest molecules into the cavities of dodecahedral cluster (Figure 2). From row of monomer guest molecules the central water molecule is the most stable in dodecahedral cluster. The same trend is observed for larger $(\text{H}_2\text{O})_{100}$ and $(\text{H}_2\text{O})_{280}$ clusters. The stabilization energies for methane and carbon dioxide in dodecahedral clusters are in qualitative agreement with the the high level theoretical calculations performed on similar 5^{12} type of water clusters^{17,18}. It is remarkable that SE decreases with the increase of cluster size. Apparently expanding of solvent shells contributes to the stabilization of the whole cluster. It should be noted that decrease in SE occurs rapidly going from $(\text{H}_2\text{O})_{20}$ to $(\text{H}_2\text{O})_{100}$ while the difference in SEs between $(\text{H}_2\text{O})_{100}$ and $(\text{H}_2\text{O})_{280}$ does not over-exceed 1 kcal/mol. Furthermore for water monomer and carbon dioxide SE reduction in first solvent shell scores to SE twice less than in $(\text{H}_2\text{O})_{20}$.

Interesting observation has been done in respect to behavior of central water molecule in cluster. We have found it relatively unbound with no essential hydrogen bonds. The possible explanation to this effect is pure electrostatic. Apparently the water molecule in the very center of icosahedral cluster entrapped in potential well. When the monomer is substituted by water dimer the same effect is observed. The hydrogen bond in water dimer strengthening upon enclosure in dodecahedral cavity. The O–O distance in water dimer becomes shorter (1.762 Å) than in isolated gas phase dimer (1.809 Å)¹⁹. The water trimer, unlikely to monomer and dimer, breaks the initial well-defined structure. Three water molecules of trimer incorporated into cavity tend to attach to the neighboring water molecules from the walls of dodecahedron thus destroying pristine trimer structure conformation. The stabilization energies for dimer and trimer guest molecules relative to separated water molecules are given in table III.

IV. CONCLUSIONS

In this theoretical study we investigated several three-dimensional structures of water clusters composed of pentamers with the dodecahedral type of organization. The largest icosahedral cluster $(\text{H}_2\text{O})_{280}$ was established as the double water shell of simple dodecahedral unit ($(\text{H}_2\text{O})_{20}$, 5^{12}), whereas first and second solvent shells included 80 and 180 water molecules respectively. The water-cooperativity effect in line of $(\text{H}_2\text{O})_{20}$, $(\text{H}_2\text{O})_{100}$, $(\text{H}_2\text{O})_{280}$

species has the linear trend. The stabilization energies of different guest molecules inside of dodecahedral cavity suggested that the guest polar water monomer does not make appreciable hydrogen bonds to the walls of the cavity, but nevertheless significantly stabilizes the 5¹² cluster without meaningful distortion of cage structure. The solvent layers has the screen effect and therefore the SE energy of inclusion of guest molecule drops down almost in two times in case of carbon dioxide and water monomer. This affect takes place already at the first solvent shell, while at the second solvent shell level the stabilization energies decrease negligibly. This can be very useful information for future investigations since it would be not necessary to include at high level of theory high-order multiple solvent layers for plausible prediction of stabilization energies of guest molecules and therefore to make computational cost inexpensive.

-
- ¹ Hori, A.; Hondoh, T. *Ann. N.Y. Acad. Sci.* **2000**, *912*, 685.
 - ² Kirov M.V.; Fanourgakis G.S.; Xantheas S.S. *Chem. Phys. Lett.* **2008**, *461*, 180.
 - ³ Fanourgakis G.S.; Apra E.; Xantheas S.S. *J. Chem. Phys.* **2004**, *2655*, 121.
 - ⁴ Shi Q.; Belair S.D.; Francisco J.S.; Kais S. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *9686*, 100.
 - ⁵ Tsai C.J.; Jordan K.D. *J. Phys. Chem.* **1993**, *97*, 5208.
 - ⁶ Wales D.J.; Hodges M.P. *Chem. Phys. Lett.* **1998**, *286*, 65.
 - ⁷ Fanourgakis G.S.; Apra E.; de Jong W.A.; Xantheas S.S. *J. Chem. Phys.* **2005**, *134304*, 122.
 - ⁸ Sloan, E.D. *Clathrate Hydrates of Natural Gases* **1998**, , 2nd ed. Marcel Dekker, New York.
 - ⁹ Chaplin M.F. *Biophysical Chemistry* **1999**, *83*, 211.
 - ¹⁰ Tegze, G.; Granasy, L.; Kvamme B. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3104.
 - ¹¹ Hartke B. *J. Chem. Phys.* **2009**, *130*, 024905.
 - ¹² Wiggins P.M. *Prog. Polym. Sci.* **1995**, *20*, 1121.
 - ¹³ Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 209.
 - ¹⁴ Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 221.
 - ¹⁵ Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M. ; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
 - ¹⁶ Khan A. *Chem. Phys. Lett.* **2000**, *319*, 440.
 - ¹⁷ Khan A. *Chem. Phys. Chem. A.* **2001**, *105*, 7429.
 - ¹⁸ Jeffrey G.A. *Inclusion Compounds* **1984**, *1*, 135. Acad. Press., Atwood J.L., Davies, J.E.D., MacNichol, D.D. Eds.
 - ¹⁹ Loboda O.A.; Goncharuk V.V.; *J. Wat. Chem. and Tech.* **2009**, *31*, 173.

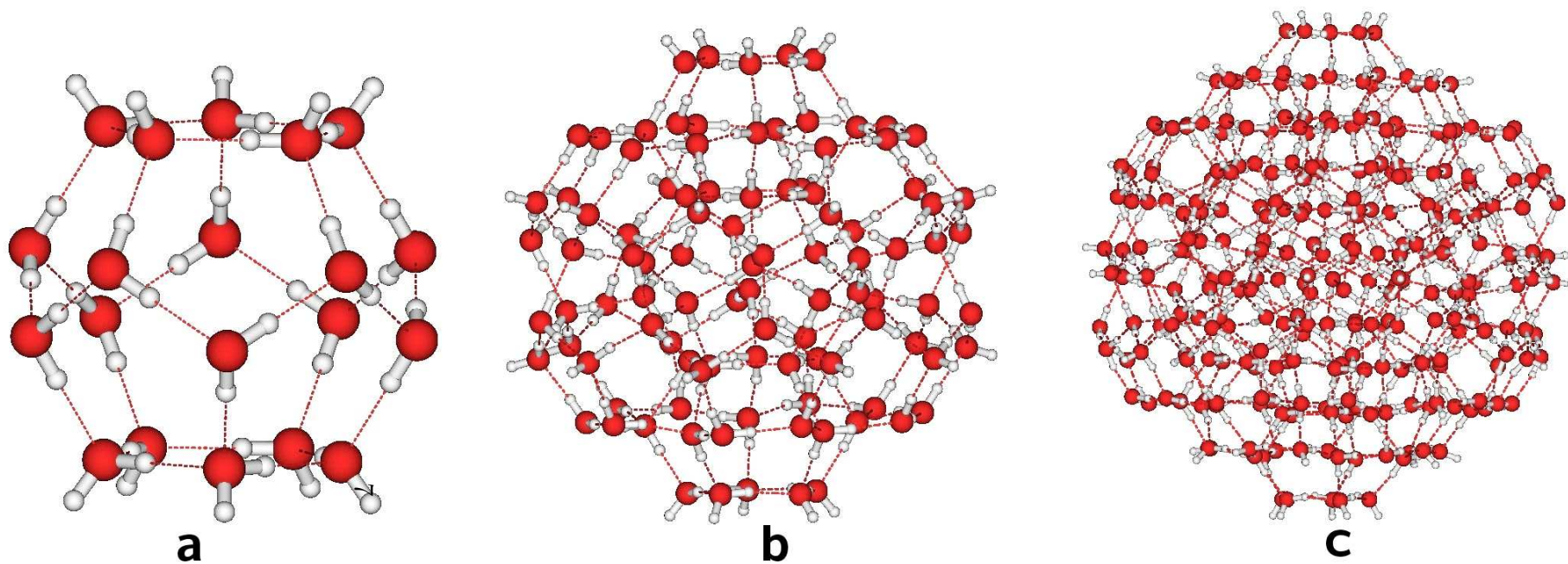


FIG. 1: Schematic representation of 5^{12} dodecahedral cluster (a) $(\text{H}_2\text{O})_{20}$, homological icosahedral (b) $(\text{H}_2\text{O})_{100}$ and (c) $(\text{H}_2\text{O})_{280}$ clusters.

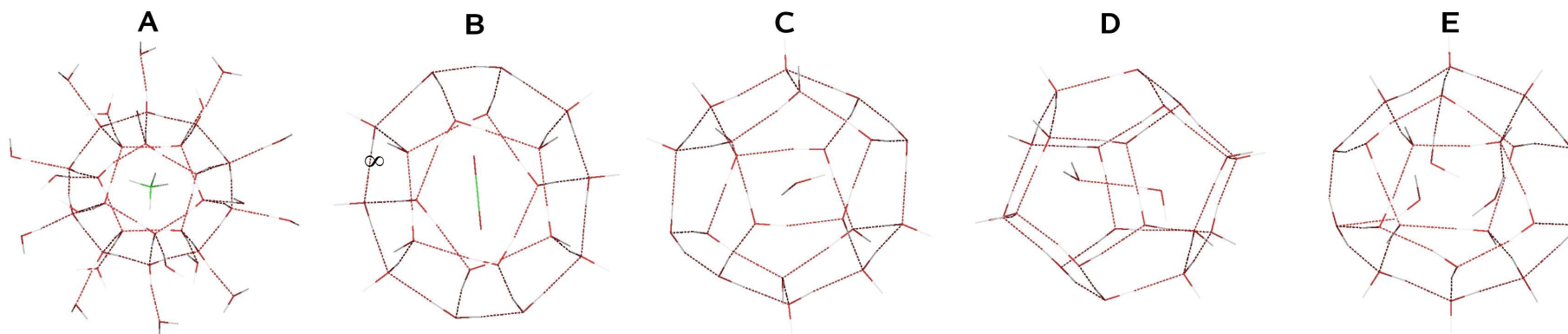


FIG. 2: Optimized structures of $M@(\text{H}_2\text{O})_{280}$. A. central dodecahedral cavity of $(\text{H}_2\text{O})_{280}$ cluster with CH_4 guest molecule, B. $\text{CO}_2@(\text{H}_2\text{O})_{280}$, C. $\text{H}_2\text{O}@(\text{H}_2\text{O})_{280}$, D $(\text{H}_2\text{O})_2@(\text{H}_2\text{O})_{280}$, E $(\text{H}_2\text{O})_3@(\text{H}_2\text{O})_{280}$. For clarity the environmental hydrogen bonds are not shown on B,C,D,E.

TABLE I: Stabilization Energies (kcal/mol), look Figure 1

| | (H ₂ O) ₂₀ | (H ₂ O) ₁₀₀ | (H ₂ O) ₂₈₀ |
|-----|----------------------------------|-----------------------------------|-----------------------------------|
| SE | -479.56 | -2995.58 | -21285.42 |
| SEP | -23.98 | -29.96 | -30.61 |

TABLE II: Stabilization energies (kcal/mol), look Figure 2

| | (H ₂ O) ₂₀ | (H ₂ O) ₁₀₀ | (H ₂ O) ₂₈₀ |
|---------------------------------|----------------------------------|-----------------------------------|-----------------------------------|
| CO ₂ | -16.81 | -7.58 | -7.15 |
| CH ₄ | -11.05 | -9.49 | -8.48 |
| H ₂ O | -22.98 | -11.33 | -11.57 |
| (H ₂ O) ₂ | -29.78 | -18.20 | -17.61 |
| (H ₂ O) ₃ | -62.64 | -18.65 | -18.29 |

TABLE III: Stabilization energies ($E(\text{H}_2\text{O})_n @ (\text{H}_2\text{O})_N - E((\text{H}_2\text{O})^*_n) - E((\text{H}_2\text{O})_N)$) (kcal/mol), look Figure 2 D,E

| | (H ₂ O) ₂₀ | (H ₂ O) ₁₀₀ | (H ₂ O) ₂₈₀ |
|---------------------------------|----------------------------------|-----------------------------------|-----------------------------------|
| (H ₂ O) ₂ | -44.18 | -32.60 | -32.01 |
| (H ₂ O) ₃ | -110.88 | -66.89 | -66.53 |