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NEUTRAL WATER CLUSTERS IN THE EARTH'S ATMOSPHERE: THE EFFECT OF ORIENTATIONAL ISOMERISM ON THEIR CONCENTRATIONS AND THERMODYNAMIC PARAMETERS

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Abstract. In order to estimate the effect of orientational isomerism on the thermodynamic parameters and concentrations of water clusters in the gas phase, all possible structures of *book*, *cage* and *prism* conformations of water hexamer (H_2O)₆ have been studied using the DFT (B3LYP/6-311++G(2d,2p)), G4, DFTB, W1BD and MB-pol calculations. It was found that taking into account of the orientational isomerism leads to the values of water cluster gas-phase concentrations different by 1–2 orders of magnitude from the results obtained when only single or several most energetically favorable structures are considered. The concentrations of all the considered hexamer structures in the saturated water vapor at $T = 298.15$ K are estimated as $1.61 \cdot 10^3$ (G4) and $8.17 \cdot 10^5$ (DFT) molecules/cm³.

Introduction. (H_2O)_n clusters are formed due to the combination of n water molecules with hydrogen bonds. For the same n , two types of isomerism can be formed: (1) the isomerism of the oxygen "skeleton" (that is the structure formed by oxygen atoms) and (2) the isomerism of the hydrogen bond network for the same skeleton, which is due to the fact that the formation of the most favorable hydrogen bond in a cluster obeys the rules similar to the Bernal–Fowler rules for an ice crystal. Two types of isomerism are shown in Fig. 1, which demonstrates the isomeric structures of the (H_2O)₆ cluster, which differ in the oxygen skeleton (Fig. 1a) and the network of hydrogen bonds for the same oxygen skeleton (Fig. 1b).

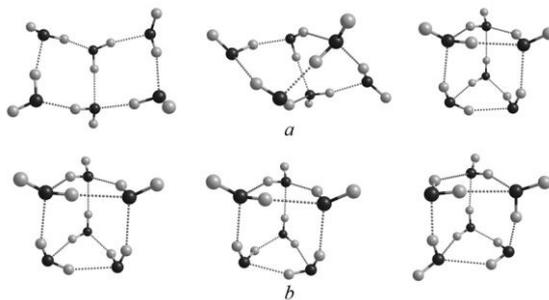


Figure 1. (a) – *book*, *prism*, and *cage* (left to right) conformations of the oxygen skeleton of (H_2O)₆; (b) – examples of orientational isomers in the *prism* conformation (H_2O)₆.

Water clusters take part in such atmospheric processes as the electromagnetic radiation propagation and chemical reactions [1–3]. As a result, multimolecular complexes of water, being contained everywhere in the Earth's atmosphere, play an important role in climate formation and change.

The structural and thermodynamic parameters of (H_2O)_n clusters with $n = 2$ –10 are currently actively studied using both experimental and theoretical methods; there are also studies of large water clusters up to 200–300 molecules in size [4]. The data obtained for (H_2O)_n clusters with $n = 3$ –5 are in good agreement with experimental studies but for larger clusters the estimates of the thermodynamic characteristics and equilibrium concentrations in the gas phase vary significantly [5–7]. In particular, the influence of the clusters' structural diversity on their thermodynamic characteristics remains unclear.

In order to estimate the effect of orientational isomerism on the thermodynamic parameters and concentrations of water clusters in the gas phase, 133 isomeric structures of water hexamer (H_2O)₆ have been studied.

Calculation details. The thermodynamic functions are calculated for 96 isomers (H_2O)₆ of *book* conformer, 27 isomers of *cage* conformer, and 10 isomers of *prism* conformer. The initial structures are selected using an original computer program generating orientational isomers for a given “skeleton” of oxygen atoms.

Full optimization of geometry and calculation of oscillation frequencies and state functions have been performed for all 133 considered isomers using DFT (B3LYP/6-311++G(2d,2p)), DFTB and G4 methods. The energy of the most stable isomers found at the DFT level was refined using the high-precision W1BD calculation. Quantum-chemical calculations were performed using the Gaussian03, Gaussian16 and DFTB+ (with mio-1-1 parameter set) programs. Analysis and visualization of the results of quantum chemical calculations were performed using the ChemCraft and Moltran programs along with a specialized software developed for these purposes.

For each cluster structure under consideration, the thermodynamic quantities E_{tot} (total energy of the molecule), $E_{\text{tot}} + \text{ZPE}$ (total energy with the zero-point energy), $U_{298\text{ K}}^0$, $H_{298\text{ K}}^0$, $G_{298\text{ K}}^0$ (the total energy with thermal corrections to the standard internal energy, enthalpy, and Gibbs energy) were calculated. Thermodynamic functions were calculated in the “rigid rotor – harmonic oscillator” approximation for the ideal-gas state of the system. Using these values, the thermodynamic functions of the cluster formation from individual molecules $\Delta_r \varepsilon$ ($\Delta_r E_{\text{tot}}$, $\Delta_r E_{\text{tot}} + \text{ZPE}$, $\Delta_r U_{298\text{ K}}^0$, $\Delta_r H_{298\text{ K}}^0$, $\Delta_r G_{298\text{ K}}^0$) were calculated.

The obtained values of thermodynamic parameters are averaged according to two schemes:

(1) the arithmetic mean:

$$\langle \Delta_r \varepsilon \rangle_{\text{av}} = \frac{1}{k} \sum_{i=1}^k \Delta_r \varepsilon_i,$$

(2) the Boltzmann average:

$$\langle \Delta_r \varepsilon \rangle_{\text{td}} = \frac{\sum_{i=1}^k \Delta_r \varepsilon_i \exp\left(-\frac{\Delta_r \varepsilon_i}{RT}\right)}{\sum_{i=1}^k \exp\left(-\frac{\Delta_r \varepsilon_i}{RT}\right)},$$

where R is the universal gas constant and T is temperature.

We analyzed also the binding energy per monomer $\Delta_b E = -\Delta_r E_{\text{tot}}/6$ and other binding thermodynamic functions per monomer.

Using the obtained values of $\Delta_r G_{298\text{ K}}^0$, the equilibrium constant of reaction $6\text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})_6$ and the concentration of clusters in the gas phase were calculated.

Additionally, the binding energy of clusters was calculated using the MB-pol model (in OpenMM software), which is positioned as superior in accuracy to all DFT models.

Results and discussion. Although three types of initial conformations were selected for optimization (*book*, *cage*, *prism*), the geometry optimization results in fourteen types of oxygen skeletons (Fig. 2). We label each cluster type as its corresponding graph indicated in the form (v, e, n) , where v is the number of vertices (here, always 6); e is the number of graph edges; n is the ordering number of the graph as presented in [8] allowing to differ the graph connectivity. The most favorable structures among them are *book*, *cage* and *prism*.

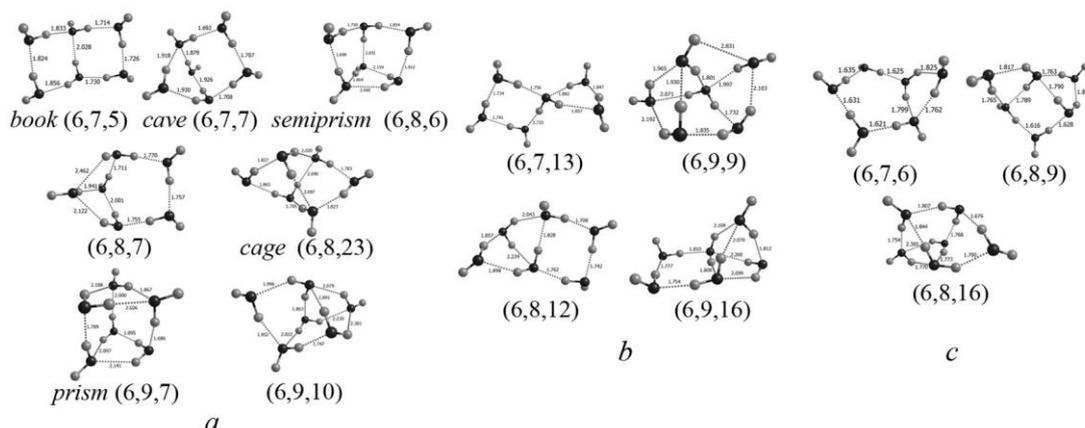


Figure 2. (a) – types of the oxygen skeletons conformations obtained after the geometry optimization of initial structures (DFT calculation), (b) – four new structures obtained from G4 calculation, (c) – three new structures obtained from DFTB calculation.

The subject of particular interest was the comparison of *ab initio* methods with MB-pol model for the set of 133 water hexamer structures. Although earlier in a number of works it was shown that MB-pol outperform all DFT

models for water molecule and small water clusters, on the average the difference between binding energies found from DFT and MB-pol calculations is within 0.5 kcal/mol (Fig. 3). This indicates a good accuracy of the chosen DFT model and its applicability for modeling the studied water clusters.

The DFTB method overestimates the cluster binding energy, which is probably due to the features of the mio-1-1 parameter set used in the work.

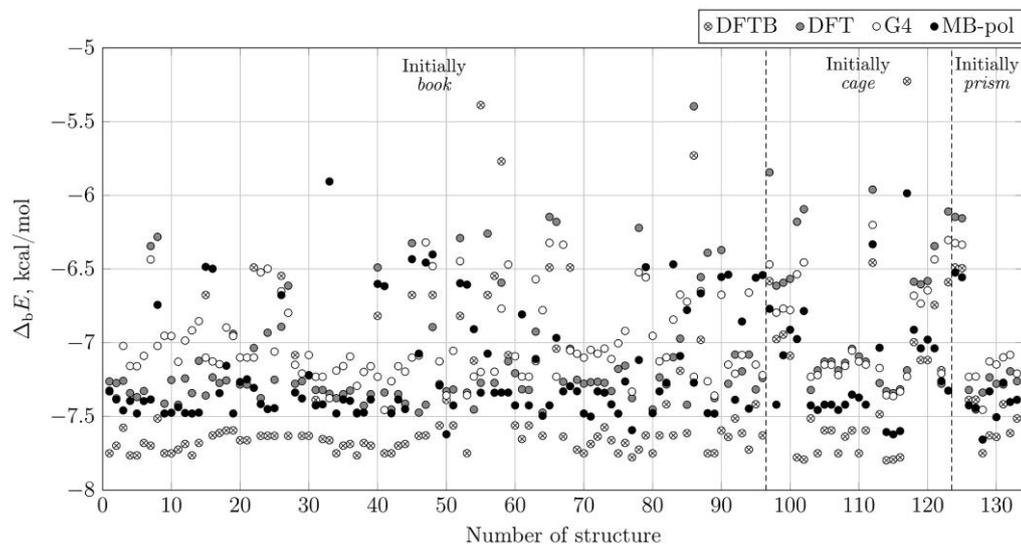


Figure 3. Binding energy for clusters found from DFTB, DFT, G4 and MB-pol calculations.

Table 1 shows the concentrations of the whole set of the located cluster structures calculated using different methods of averaging. Namely, this gives the values of concentrations calculated as a sum of concentrations found for each optimized cluster in separate (C_{sum}); the concentration C_{min} calculated on the basis of minimum energy cluster only (as if all clusters consisted only from the most favorable clusters); the concentrations C_A calculated on the basis of the arithmetic mean values; and concentration C_B calculated on the basis of Boltzmann averaging. Additionally, the values of relative concentrations in percent are given as the ratio of C_{sum} concentration to the concentration of monomeric molecules in a saturated water vapor $C_{\text{H}_2\text{O}}$.

Table 1. Concentrations of clusters of all considered types (molecules/cm³) estimated by various averaging methods at different theory levels. Thermodynamic conditions: ideal gas state at $T = 298.15$ K and monomer pressure 3200 Pa ($P^0 = 10^5$ Pa).

	C_{sum}	C_{min}	C_A	C_B	$C_{\text{sum}}/C_{\text{H}_2\text{O}}, \%$
DFT	$8.17 \cdot 10^5$	$2.82 \cdot 10^4$	$6.10 \cdot 10^2$	$2.88 \cdot 10^3$	$1.05 \cdot 10^{-10}$
G4	$1.61 \cdot 10^3$	$1.37 \cdot 10^2$	$7.99 \cdot 10^{-1}$	$2.91 \cdot 10^0$	$2.07 \cdot 10^{-13}$
DFTB	$1.68 \cdot 10^9$	$9.35 \cdot 10^7$	$1.88 \cdot 10^5$	$3.78 \cdot 10^6$	$2.16 \cdot 10^{-7}$

As is evident from the Table, the C_{sum} concentrations are always higher than others. The minimum values are obtained for C_{min} concentrations due to the fact that this concentration does not take into account the number of isomers arising within this oxygen skeleton. However, if the number of isomers will be accounted (C_{min} is multiplied by 133), this value is higher than other concentrations. The last method is, however, not used in practice. Usually, the concentrations are calculated on the basis of single isomer which is considered as one of the most favorable ones. As is evident from the Table, such method results in the significant underestimation by one or two orders of magnitude.

The arithmetic and Boltzmann averaging result in the significantly higher values. The arithmetic-based averaging gives typically lower values. This is in agreement with an idea that this estimates the system which is far from equilibrium. At the same time, the Boltzmann averaging gives the values closest to the concentrations estimated by direct summation of separate isomer concentrations. In the last case, the difference between these methods is typically within one order of magnitude.

It should be noted that the final concentrations are extremely dependent on the quantum chemical calculation method. Among these methods, DFTB gives highest concentrations of $2.16 \cdot 10^{-7}\%$ for hexamers. At the same time, DFT and G4 give the concentrations of $1.05 \cdot 10^{-10}$ and $2.07 \cdot 10^{-13}$ % relatively to the concentrations of water vapor molecules. Among these values, first one coincides better with the W1BD estimates for selected clusters. Because

WIBD is considered as theory providing higher accuracy for the test set of molecules, to our opinion, the DFT result should be considered as the most reliable estimate.

Figure 4 shows the concentrations of separate types of isomers calculated with different quantum chemistry methods. In agreement with the calculated Gibbs free energies, the highest concentration takes place for the *book* isomer (6,7,5). This takes place for all the considered theory levels and for all the used methods of averaging. The concentrations of other structures rapidly decline by two-three orders of magnitude and more. In the case of DFT calculations, only *cave* isomers (6,7,7) have the comparable concentrations which is, however, half-order of magnitude lower than the concentration of *book*.

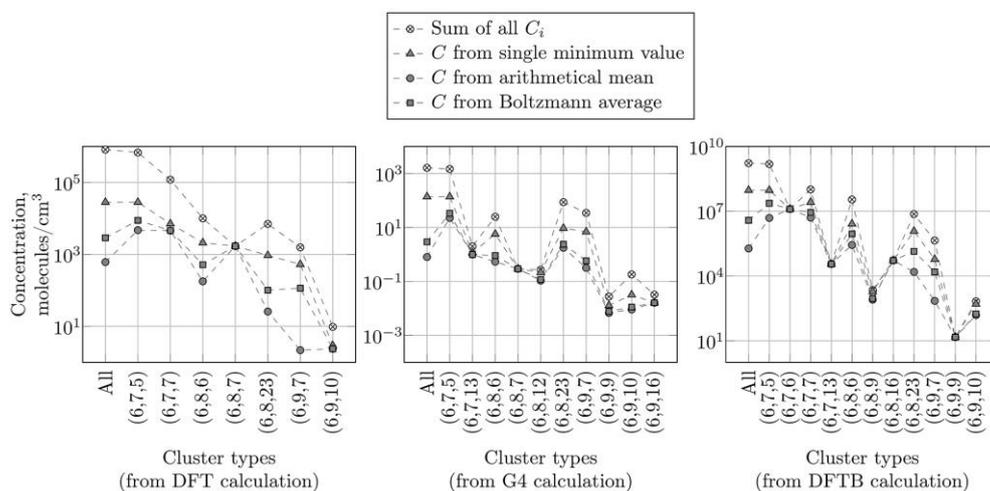


Figure 4. Concentrations of clusters of various kinds calculated with different weighting methods.

Conclusion. The existence of a large number of isomeric multimolecular water complexes makes a significant contribution to their concentration in the gas phase. The more molecules in a cluster, the more significant the influence of orientational isomerism on cluster concentration, therefore, to calculate the concentrations of clusters of several molecules, it is necessary to take into account the phenomenon of orientational isomerism. At the same time, the standard approach, in which the concentration is calculated only for the most energetically profitable structure, leads to an underestimation of the concentration by 1–2 orders of magnitude.

Of the considered types of oxygen skeletons, the greatest concentration in the gas phase is observed in the structure *book*. This is achieved primarily due to the greater number of possible isomers compared with *cage* and *prism*.

The concentrations of all the considered hexamer structures in the saturated water vapor at 298.15 K are estimated as $1.61 \cdot 10^3 \text{ cm}^{-3}$ (G4) and $8.17 \cdot 10^5 \text{ cm}^{-3}$ (DFT).

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