Modelling thermodynamic properties of mixed ozone and argon hydrates using quantum chemistry methods

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Abstract. Ozone is a gas in demand in industry and medicine. The issue of its storage is acute so far and is connected with the search for the most suitable second guest gas enhancing ozone storage. This paper is devoted to the study of the stability of the SI and SII cage structures in the presence of a mixture of ozone and argon using the density function method. Carried out modeling allowed finding stable molecular structures and determining the thermodynamic conditions of hydrate stability for the O\textsubscript{3}+Ar gas mixture. In addition the electron density distribution and stabilization energies were calculated that could be useful in experimental investigation.

1. Introduction

Ozone is a powerful oxidant that provides its wide applicability in medicine and industry. At the same time its high oxidising potential poses a danger due to the formation of free oxygen radicals in many reactions that determines its high toxicity. The importance of the applications and the high rate of ozone decay in general require the development of a long-term storage technology for ozone. However there were no effective methods for ozone storing: the half-life time of ozone being dissolved in water was about 20-30 min at \textasciitilde 20°C \cite{1,2} and about 1-2 days in the water frozen after that to \textasciitilde 18°C \cite{3}.

In 1964, the idea of storing ozone encaged in clathrate hydrates was presented \cite{4}. Authors offered to use the carbon tetrachloride (CCl\textsubscript{4}) to decrease the formation pressure of O\textsubscript{3}+CCl\textsubscript{4} double hydrate of structure SII as a “help-guest substance”. This work opened up the possibility of finding other guest substances to produce mixed hydrates containing ozone. Recent experimental results show that the clathrate hydrate of O\textsubscript{3}+O\textsubscript{2}+CCl\textsubscript{4} or O\textsubscript{3}+O\textsubscript{2}+Xe or O\textsubscript{3}+O\textsubscript{2}+CO\textsubscript{2} mixtures can preserve ozone at a mass fraction of about 0.1% for over 20 days under atmospheric pressure \cite{5,6}.

The search for the help-guest gas that may provide the most efficient ozone storage is still ongoing. Analytical theories of clathrate compounds allow determining the stability regions of gas hydrate i.e. to build the P-T diagrams for every specific gas mixture compositions. These theories are based on the van der Waals-Platteeuw theory \cite{7} allowing guest-guest interaction \cite{8} and multiple occupancy \cite{9}. The authors of work \cite{10} used statistical-thermodynamic approach to predict the increase of ozone content in hydrate when the nitrogen is added to the gas mixture. By the use of first-principles \cite{11} and lattice dynamics calculation the electronic, structural, dynamic and thermodynamic properties of Ar clathrate hydrates of SI, sH and tetragonal structure were studied \cite{12}. An agreement with the experimental data \cite{13} was obtained.
In present work the structural and thermodynamic properties of molecular clusters of mixed O$_3$+Ar hydrates of SI and SII structures were investigated using the density function method (DFT) to find equilibrium structures and stabilization energy as well as to describe the thermodynamic stability of multicomponent systems containing ozone and argon. The main aim of this work is to reveal the nature of the increased stability of ozone molecules in hydrates and to find the conditions for the formation of mixed hydrates of ozone.

2. Methods
The structure of molecular clusters under consideration consists of only those water molecules that form small and large cavity polyhedrons: 5$^{12}$ and 5$^{12}$6$^2$ of SI, 5$^{12}$ and 5$^{12}$6$^4$ of SII. The following structures were studied: 5$^{12}$, 5$^{12}$6$^2$, 5$^{12}$6$^4$, 1O$_3$@5$^{12}$+nAr@5$^{12}$6$^2$ (one ozone molecule occupies 5$^{12}$ cavity and n argon atoms occupy 5$^{12}$6$^2$ cavity and so on), Ar@5$^{12}$+1O$_3$@5$^{12}$6$^2$, 1O$_3$@5$^{12}$+nAr@5$^{12}$6$^4$, Ar@5$^{12}$+1O$_3$@5$^{12}$6$^4$. These structures were optimized using the hybrid potential of electron DFT B3LYP and potential MP2 with 6-311G bases and Gaussian 09 software package [14] that allows calculating the Hibi's energy as well as entropy and enthalpy. Stabilization energies and hydrogen bond (H-bond) energies were calculated using algorithms presented in [15]. Water molecules were considered as rigid so the values of intramolecular O-H lengths and H-O-H angles were fixed throughout the simulation time. Small cages of corresponding hydrate structure (@SI or @SII) are labeled by ‘S’, large – ‘L’. Empty cages are labeled ‘Em’.

3. Results and discussion
Figure 1 presents the snapshots of optimized cluster structures O$_3$L+ArS@SI, EmL+ArS@SI, EmL+EmS@SI, O$_3$L+EmS@SI.

![Figure 1](image1.png)

Figure 1. Optimized structures of cluster contain 2 different cavities - large (L, 5$^{12}$6$^2$) and small (S, 5$^{12}$) cages: EmL+ArS@SI (a); O$_3$L+EmS@SI (b), EmL+EmS@SI(c), and O$_3$L+ArS@SI(d).

Figure 2 shows the snapshots of optimized cluster structures O$_3$L+ArS@SII, EmL+ArS@SII, EmL+EmS@SII, O$_3$L+EmS@SII.
Figure 2. Optimized structures of cluster contain 2 different cavities - large (L, \(5^{12}_{16}\)) and small (S, \(5^{12}\)) cages: Eml+ArS@SII (a); O\(_3\)L+EmS@SII (b), EmL+EmS@SII (c), and O\(_3\)L+ArS@SII (d).

The energy of stabilization of clusters: O\(_3\)L+ArS@SI, EmL+ArS@SI, EmL+EmS@SI, O\(_3\)L+EmS@SI and that of: O\(_3\)L+ArS@SII, EmL+ArS@SII, EmL+EmS@SII, O\(_3\)L+EmS@SII were calculated. The interaction energy of O\(_3\) with the lattice of a large cavity of SI hydrate is higher than with that of SII hydrate and is -6.56124456 kcal/mol at \(T = 273.15\) K and \(P = 1.5\) MPa. Using \textit{ab initio} methods the influence of argon on the configuration of a small cavity SI, SII was also estimated. The stabilization energies are summarized in Tables 1, 2.

Table 1. Energy, stabilization energy (SE), relative to separated constituent molecules, SE/monomer (SEP) and H-bond energy. The SE energy values are calculated at MP2/6-311G, B3LYP/6-311G level for all clusters.

| Cluster         | Energy values B3LYP/6-311G, Hartree | Energy values MP2/6-311G, kcal/mol | SE, kcal/mol | SEP, kcal/mol | H-bond, kcal/mol |
|-----------------|-------------------------------------|-----------------------------------|--------------|---------------|-----------------|
| O\(_3\)L+ArS@SI| -3733.329955                        | -3721.971484                      | -358.07      | -9.18         | -5.87           |
| EmL+ArS@SI      | -3507.930396                        | -3497.189049                      | -324.52      | -8.32         | -5.32           |
| EmL+EmS@SI      | -2980.383351                        | -2970.389748                      | -362.95      | -9.30         | -5.95           |
| O\(_3\)L+EmS@SI| -3205.782074                        | -3195.102969                      | -357.46      | -9.16         | -5.86           |
| H\(_2\)O        | -76.392861                          | -76.149009                        |              |               |                 |
| O\(_3\)         | -225.388267                         | -224.711970                       |              |               |                 |
| Ar              | -527.551910                         | -526.852543                       |              |               |                 |
Table 2. Energy, stabilization energy (SE), relative to separated constituent molecules, SE/monomer (SEP) and H-bond energy. The SE energy values are calculated at MP2/6-311G, B3LYP/6-311G level for all clusters.

| Cluster       | Energy values          | Energy values          | SE, kcal/mol | SEP, kcal/mol | H-bond, kcal/mol |
|---------------|------------------------|------------------------|--------------|---------------|------------------|
|               | b3lyp/6-311G, Hartree   | MP2/6-311G, Hartree    |              |               |                  |
| O₃L+ArS@SII   | -4038.927181           | -4026.600157           | -378.55      | -8.01         | -5.65            |
| EmL+ArS@SII   | -3813.532545           | -3801.885067           | -387.26      | -8.20         | -5.78            |
| EmL+EmS@SII   | -3285.983149           | -3275.045878           | -400.66      | -8.43         | -5.98            |
| O₃L+EmS@SII   | -3511.377745           | -3499.744359           | -385.92      | -8.17         | -5.76            |
| H₂O           | -76.392861             | -76.149009             |              |               |                  |
| O₃            | -225.388267            | -224.711970            |              |               |                  |
| Ar            | -527.551910            | -526.8525438           |              |               |                  |

The argon-ozone interaction energy in the O₃L+ArS@SI cluster equals -4.033007 kcal/mol (see Table I) and O₃L+ArS@SII equals to -2.419166 kcal/mol (see Table 2). It was demonstrated that the interaction energy: argon-S@SI, ozone-L@SI is about 3.05283615 and -6.56124456 kcal/mol, respectively. The interaction energies argon-S@SII, ozone-L@SII are about 1.577560 and -3.971510 kcal/mol, respectively. Despite the resulting value of the argon-S interaction energy, one can speak of the hydrate formation since the energy of this interaction is much lower than that of the hydrogen bonds that support the integrity of the cluster structure.

Table 3 presents data on the average charge distribution for all optimized clusters presented in Figures 1 and 2. The average charges on the atoms of oxygen and hydrogen in the empty cluster EmLS@SI, O₃L+ArS@SI are -0.835940|e| and +0.417970|e|, -0.858363|e| and +0.429182|e|, respectively.

| Cluster       | q₀, |q₀, | Cluster       | q₀, |q₀, |
|---------------|----|----|---------------|----|----|
| O₃L+ArS@SII   | -0.858363 | +0.429182 | O₃L+ArS@SII   | -0.817945 | +0.408972 |
| EmL+ArS@SII   | -0.848188 | +0.424094 | EmL+ArS@SII   | -0.839856 | +0.419928 |
| EmL+EmS@SII   | -0.835940 | +0.417970 | EmL+EmS@SII   | -0.849874 | +0.424937 |
| O₃L+EmS@SII   | -0.825273 | +0.4126365| O₃L+EmS@SII   | -0.835678 | +0.417839 |

The charges of oxygen and hydrogen atoms of clusters are calculated by the methods of quantum mechanics and differ by an average of 4% from the thermodynamic properties used for calculating the SPC/E potential. The possibility of formation of weak chemical bonds between host and guest molecules is determined. The data on the value of hydrogen bonds are given in Tables 1, 2.

The average charges on oxygen and hydrogen atoms in EmL+ArS@SI, O₃L+EmS@SI clusters have also been calculated. It is shown that the electron density in clusters varies insignificantly, and the structure remains stable in all the systems that are outlined in the work.
4. **Conclusions**

Calculated stabilization energies and energies of interaction between guest gases and hydrate H$_2$O lattice show the possibility of stabilizing clusters consisting of large and small cavities of SI, SII hydrates, i.e. the formation possibility of double O$_3$+Ar SI or SII hydrate at $T = 273.15$ K and $P = 1.5$ MPa.

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