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Stability of $O_3 + N_2$, $O_3 + O_2$ and $O_3 + CO_2$ double hydrates: DFT study

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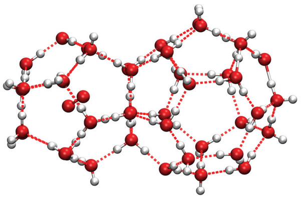
The possibility of formation of double $O_3 + N_2$, $O_3 + O_2$, $O_3 + CO_2$ hydrates and their structural and energetic properties have been estimated using the DFT calculations in order to expand the hydrate application in ozone storage technology. It was shown that N_2 is the most suitable helper gas that could stabilize water framework in the presence of ozone.



A wide applicability of ozone in medicine, industry, agri- and aquacultures arises from its very high oxidation potential that is provided by the molecular decay and accompanied by the formation of toxic free radicals. Currently, there is no efficient method for a long-term storage of ozone. Gas hydrate formation is a promising technology for ozone and ozone-based gas mixtures storage due to the possibility of single O_3 molecule incorporation into a cavity of ~1 nm mean size that slows down O_3 dissociation. For example, CCl_4, O_2, Xe, and CO_2 may be employed as helper gases for double and triple mixtures with O_3 in order to reach acceptable temperature and pressure conditions of hydrate formation and to accommodate a larger O_3 content.[1–3]

It has been experimentally found that one of the highest mass fractions of ozone trapped in a hydrate can reach 2.15 wt% in the case of $O_3 + O_2 + CO_2$ mixture.[4] However, this value could be significantly increased through continuous hydrate formation of pure ozone.[5] Thus, the search for the set of helper gases is still ongoing.

This work was aimed at the estimation of stability of mixed $O_3 + N_2$, $O_3 + O_2$, and $O_3 + CO_2$ hydrate cavities (clusters) in cubic structures **sI** and **sII** using DFT calculations. The studied clusters represent the molecular structure of small (marked herein as ‘S’) and large (denoted as ‘L’) cavities filled with O_3 and ‘Gas’ (N_2, O_2, or CO_2). Empty cavities are marked as ‘Em’. Due to the size of guest molecules, the following clusters were simulated: EmS + EmL, GasS + EmL, EmS + O_3L and GasS + O_3L moieties of both structures **sI** and **sII**. These structures consist of 39 H_2O molecules forming 61 hydrogen bonds (H-bonds) in the case of **sI** clusters and of 43 H_2O molecules and 67 H-bonds in the case of **sII** clusters. Structure optimization and frequency calculation were carried out by the DFT method implemented in Gaussian 9 software[6] using B97D functional and 6-31++G(d,p) basis set. This combination provides accurate qualitative energy data for H-bonding systems including water clusters.[7–9] The energy (Table S1 in Online Supplementary Materials), geometry parameters (Table S2) and optimized structures (Figure 1 for N_2S + O_3L **sII** and more in Table S3) were determined. The frequency calculations performed for all the structures have revealed that all the eigenvalues of Hessian matrix are positive, and hence, the corresponding frequencies are real. This means that these structures are indeed in minima (at least local). Computational algorithms for the stabilization energy and that per monomer (SEP) were reported earlier.[10,11] The H-bonding energies (HBE) were calculated for empty and non-empty clusters after the removal of guest molecules. In these cases, the corresponding stabilization energy values were divided by the number of H-bonds. The removal of guest molecules allows one to exclude their contribution *via* van der Waals interactions to the cluster energy and HBE. The energy (E_{int}) of interaction between guest molecules and the H_2O framework was calculated as a difference between the energy of H_2O cluster with guest molecules (E_{cluster}) and the sum of energies of the empty cluster (E_{empty}) and guest molecules ($n \cdot E_{\text{guest}}$), where n was the number of guest molecules inside the H_2O cages. The deformation energy (E_{def}) reflecting the water framework distortion was calculated as a difference between the energies of filled clusters with guest molecules being removed after the structure optimization ($E_{\text{no guest}}$) and the energies of empty water clusters (E_{empty}). A positive E_{def} value indicates that the water framework is being unstable.

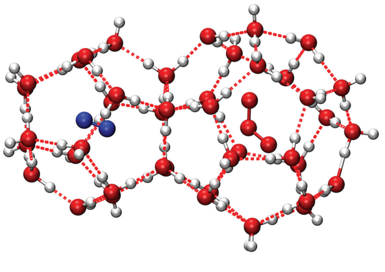


Figure 1 Optimized structure of N_2S + O_3L moiety in **sII** hydrate.

Data on the hydrate cluster stabilization energy per monomer and H-bonding energy are summarized in Table 1. The comparison of SEP values for clusters of **sI** and **sII** moieties has clearly shown that the empty structures are more stable due to the highest SEP values. It was found that the SEP energies were decreased upon an addition of the guest molecules. The SEP energy of EmS + O_3L clusters is the closest to those estimated for the empty structures due to the H-bonding interaction of each H_2O molecule with surrounding molecules, while the guest molecules interact with water framework and other guests *via* weak van der Waals interactions. As was expected, the small guest molecules such as N_2 and O_2 weakly affect the structures

Table 1 Calculated SEP and HBE values (in kcal mol^{-1}).

Cluster	SEP (**sI**)	HBE (**sI**)	SEP (**sII**)	HBE (**sII**)
EmS + EmL	–9.03	–5.78	–8.90	–5.72
O_2S + EmL	–8.87	–5.77	–8.73	–5.68
CO_2S + EmL	–8.90	–5.76	–8.75	–5.67
N_2S + EmL	–8.88	–5.77	–8.74	–5.68
EmS + O_3L	–8.97	–5.75	–8.79	–5.65
O_2S + O_3L	–8.81	–5.75	–8.61	–5.61
CO_2S + O_3L	–8.79	–5.73	–8.70	–5.64
N_2S + O_3L	–8.83	–5.74	–8.68	–5.65

and H-bonding interactions of water frameworks. The CO_2 and O_3 molecules demonstrate a larger interaction effect that leads to a more significant impact on the cluster structure. These results are in agreement with the calculated E_{def} values (Table 2), whose positive sign means that $|E_{\mathrm{empty}}|$ is higher than $|E_{\mathrm{no\ guest}}|$ independently of the chosen gas content. The $|E_{\mathrm{def}}|$ values for N_2S + EmL and O_2S + EmL clusters revealed their least difference from the empty structure as compared to the CO_2- and O_3-containing clusters. The obtained HBE values are also consistent with the experimental data reported previously (–5.44 ± 0.70 kcal mol^{-1}).[12]

Every E_{int} value is negative, thus showing the attractive interaction between the guest and host molecules. Moreover, these values for single O_2, CO_2 and N_2 molecules are lower than the HBE values. The E_{int} values for a single O_3 guest are comparable with HBE, whereas each H_2O molecule forms several H-bonds. This means that the guest molecules could not destroy or significantly deform the water cluster structures. In the case of single guest occupation of water cluster represented by a single dodecahedral cage, the recent Møller-Plesset (MP2) perturbation theory calculations with the same basis set resulted in the –2.58 (N_2), –6.42 (O_2) and –3.39 kcal mol^{-1} (CO_2) values of guest–host interaction energies,[13] and in the case of similar structures (EmS + + O_3L) with other functional and basis set calculations resulted in –6.56 (O_3 **sI**) and –3.97 kcal mol^{-1} (O_3 **sII**)[14] values, which are close to values obtained in the present work. The larger difference observed for O_2 guest may be explained by an electronic state of oxygen molecule (in our case, the triplet state). Thus, the E_{int} for singlet O_2 state (O_2S + EmL) was also calculated. The values of interaction energy for O_2 molecules in their singlet state were: –6.93 and –4.18 kcal mol^{-1} for **sI** and **sII** moieties, respectively. This agrees with the above value of –6.42 kcal mol^{-1}. Moreover, in the case of single cage, the guest–host interaction leads to a homogeneous contraction of the whole water cluster. However, such a contraction could not be uniform since the ‘5^{12} cage’ is connected through its penta-ring to a large cage. This may also explain the energy differences of guest–host interactions calculated for the water clusters presented in **sI** and **sII** moieties with the same gas content.

The negative value of $\{E_{\mathrm{int}}(\mathrm{GasS} + O_3\mathrm{L}) - [E_{\mathrm{int}}(\mathrm{GasS} + \mathrm{EmL}) + + E_{\mathrm{int}}(\mathrm{EmS} + O_3\mathrm{L})]\}$ could indicate an effect of the second guest molecule on the stabilization of EmS + O_3L clusters. These values are 0.13 and 0.3 kcal mol^{-1} (O_2S + O_3L), 2.29 and –2.67 kcal mol^{-1} (CO_2S + O_3L), –0.34 and –2.53 kcal mol^{-1} (N_2S + O_3L) for **sI** and **sII** clusters, respectively. These results show that the addition of N_2 as the second guest leads to a larger stabilization effect on the formation of O_3 hydrate.

Table 2 Calculated E_{int} and E_{def} values (in kcal mol^{-1}).

Cluster	E_{int} (**sI**)	E_{def} (**sI**)	E_{int} (**sII**)	E_{def} (**sII**)
O_2S + EmL	–2.61	+0.21	–1.03	+2.48
CO_2S + EmL	–3.87	+0.81	–2.04	+3.30
N_2S + EmL	–2.97	+0.30	–1.38	+2.52
EmS + O_3L	–6.60	+1.38	–3.90	+4.49
O_2S + O_3L	–9.08	+1.56	–4.63	+7.07
CO_2S + O_3L	–8.18	+2.61	–8.61	+5.40
N_2S + O_3L	–9.91	+2.13	–7.81	+4.62

In summary, the analysis of calculated stabilization energies, guest–host interactions, and deformation energies suggests that the N_2 molecules are the most suitable helper gas to form the double ozone-based hydrate. Small N_2 molecules do not deform water frameworks and also stabilize them in the presence of O_3 in the large cage. This is in a good agreement with the recent thermodynamic data[1] acquired in the work, where it was found that N_2 could be used for increasing the ozone content in hydrates, and the ozone storage amount in the O_3 + O_2 + N_2 + CO_2 hydrate could be at least several times higher than that for the experimentally described O_3 + O_2 + CO_2 gas hydrates. The molecule CO_2 is large and can also occupy the large cages. This may lead to a significant reduction of O_3 amount in hydrate form.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.11.036.

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