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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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Energy parameters

Table S1 Energies of optimized hydrate clusters.[a]

Structure	Energy/Hartrees
H_2O	–76.3928315053 (–76.371942)
O_3	–225.317298041 (–225.310584)
O_2 triplet	–150.252381009 (–150.248829)
CO_2	–188.481885686 (–188.470649)
N_2	–109.460327554 (–109.454917)

Cluster **sI**	Full Energy	No Guest	Cluster **sII**	Full Energy	No Guest
EmS + EmL	–2980.05341764 (–2979.067123)		EmS + EmL	–3285.68869017 (–3284.603843)	
O_2S + EmL	–3130.31080889 (–3129.320108)	–2980.05302696 (–2979.066777)	O_2S + EmL	–3435.94206014 (–3434.854308)	–3285.68341191 (–3284.599892)
CO_2S + EmL	–3168.54240342 (–3167.543939)	–2980.05147588 (–2979.065815)	CO_2S + EmL	–3474.17452118 (–3473.077748)	–3285.68290162 (–3284.598590)
N_2S + EmL	–3089.51934364 (–3088.526780)	–2980.05290659 (–2979.066628)	N_2S + EmL	–3395.15073066 (–3394.060956)	–3285.68336276 (–3284.599830)
EmS + O_3L	–3205.38164334 (–3204.388221)	–2980.05114022 (–2979.064907)	EmS + O_3L	–3511.01222676 (–3509.920643)	–3285.68082753 (–3284.596690)
O_2S + O_3L	–3355.63917559 (–3354.641012)	–2980.05093314 (–2979.064617)	O_2S + O_3L	–3661.26677258 (–3660.170640)	–3285.67694230 (–3284.592571)
CO_2S + O_3L	–3393.86730376 (–3392.861387)	–2980.04909063 (–2979.062951)	CO_2S + O_3L	–3699.50351469 (–3698.398793)	–3285.68026475 (–3284.595239)
N_2S + O_3L	–3314.84893230 (–3313.848411)	–2980.05024143 (–2979.063711)	N_2S + O_3L	–3620.47942968 (–3619.381787)	–3285.68068255 (–3284.596486)

[a] Values in parentheses belongs to ZPE corrected. The O_2 values correspond to its triplet state.

Geometry parameters

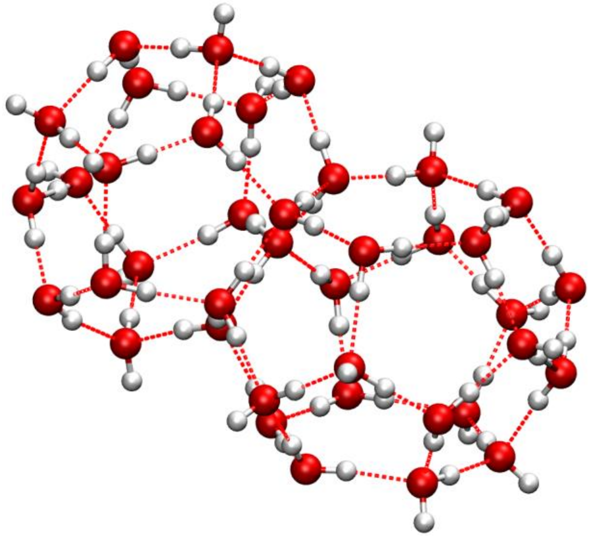
The O–H distances in H_2O molecules vary in the range from 0.967 to 1.03 Å. There is no significant change in the short-range order of H_2O molecules and their geometry upon the inclusion of guest molecules. Analogous conclusions were made in another work.[S1] However, the cluster dissymmetry leads to a slight non-uniform cage deformation that is the reason for diameter values ranging.

Table S2 Average O–O distances (Å) and O–H–O angles (degrees) in the water framework and diameters (D) of the small and large cavities (Å).

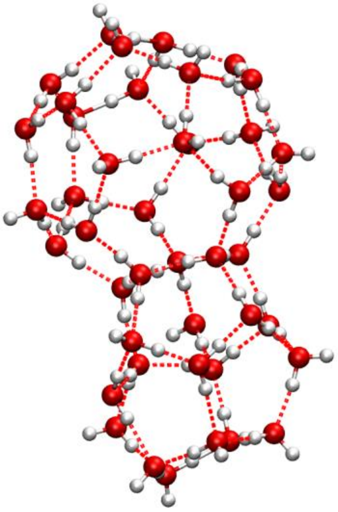
Cluster	sI				sII			
	O···O	O–H···O	D_{small}	D_{large}	O···O	O–H···O	D_{small}	D_{large}
EmS + EmL	2.747	174.14	7.4–7.6	8.1–8.2	2.743	174.27	7.3–7.4	8.8–9.0
O_2S + EmL	2.750	174.35	7.3–7.5	8.1–8.2	2.748	172.99	7.6–7.7	8.9–9.1
CO_2S + EmL	2.754	174.37	7.3–7.7	8.2–8.6	2.753	174.60	7.4–7.9	8.8–9.1
N_2S + EmL	2.750	174.38	7.4–7.6	8.1–8.3	2.748	172.95	7.6–7.7	8.7–9.0
EmS + O_3L	2.745	174.24	7.4–7.5	8.1–8.5	2.744	172.90	7.6–7.7	8.9–9.1
O_2S + O_3L	2.748	174.42	7.3–7.6	8.2–8.4	2.749	174.18	7.7–7.8	8.8–9.2
CO_2S + O_3L	2.755	173.04	7.4–7.9	8.7–8.9	2.751	174.60	7.3–7.8	8.9–9.2
N_2S + O_3L	2.748	174.34	7.3–7.5	8.6–8.7	2.744	172.98	7.6–7.7	8.7–9.1

Optimized structures

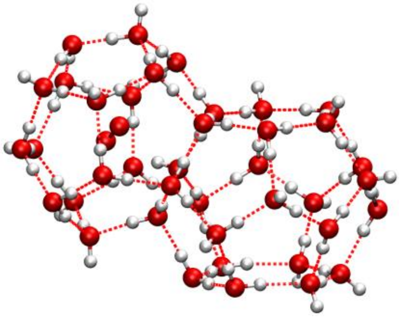
Table S3 Optimized $5^{12}+5^{12}6^{2}$ and $5^{12}+5^{12}6^{4}$ clusters containing N_2, O_2 and CO_2 in the small cavities, O_3 in large cavities and empty structures. The O_2 molecules are in the triplet state.

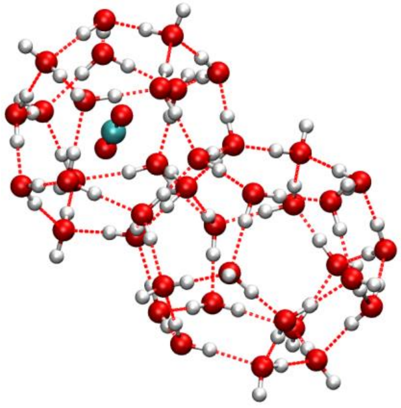


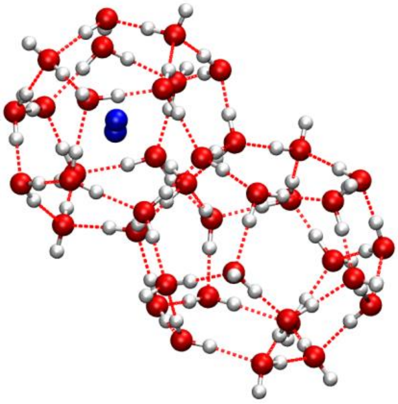
Empty **sI**



Empty **sII**



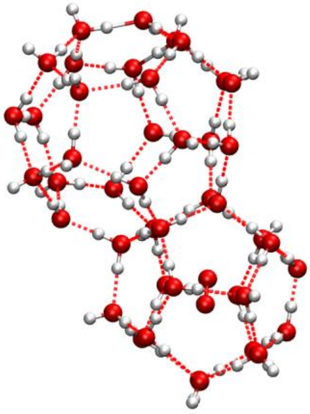


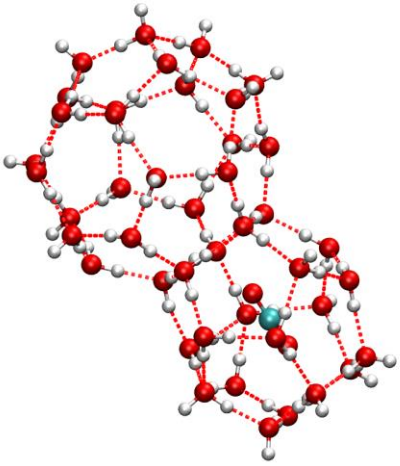


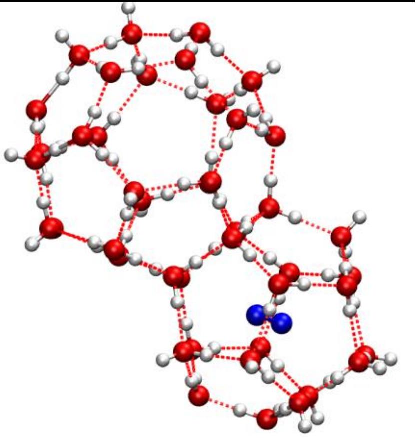
O_2S + EmL (**sI**)

CO_2S + EmL (**sI**)

N_2S + EmL (**sI**)



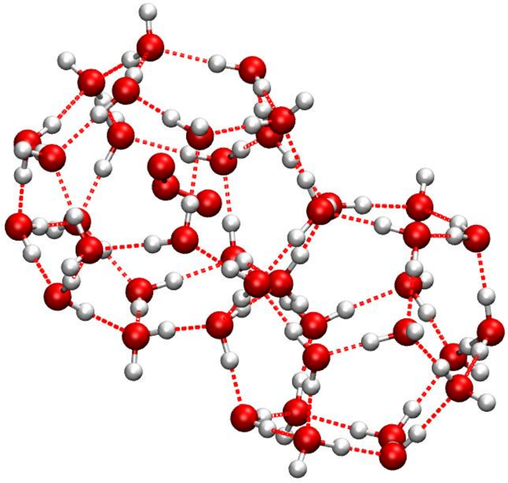


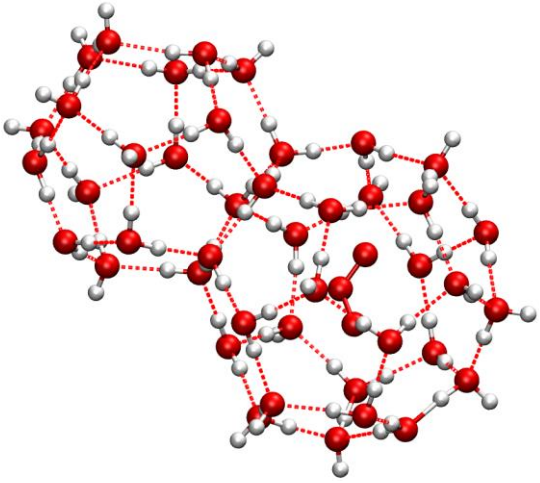


O_2S + EmL (**sII**)

CO_2S + EmL (**sII**)

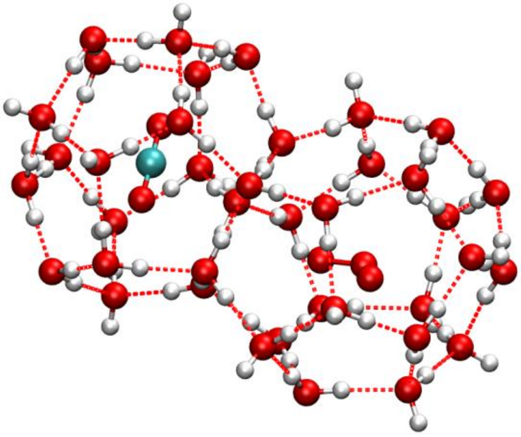
N_2S + EmL (**sII**)

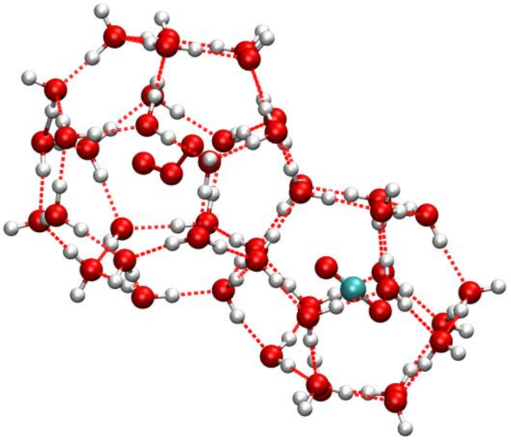




EmS + O_3L (**sI**)

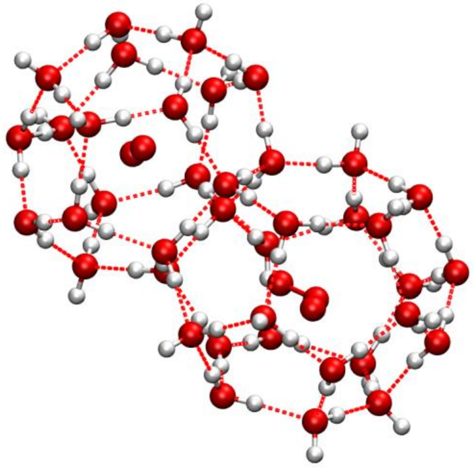
EmS + O_3L (**sII**)



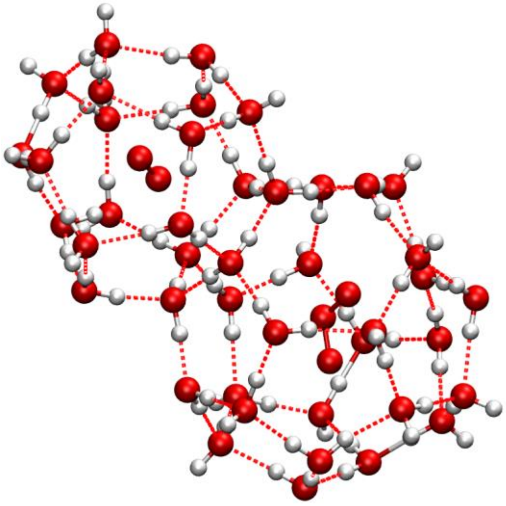


CO_2S + O_3L (**sI**)

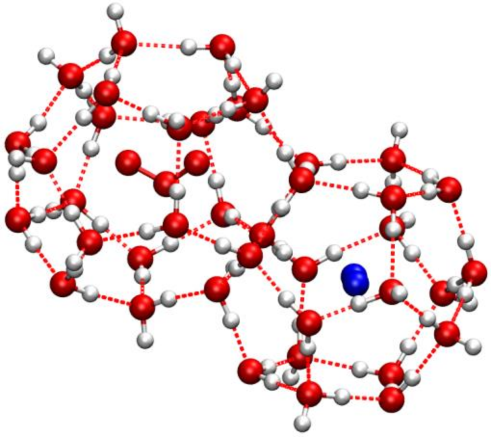
CO_2S + O_3L (**sII**)



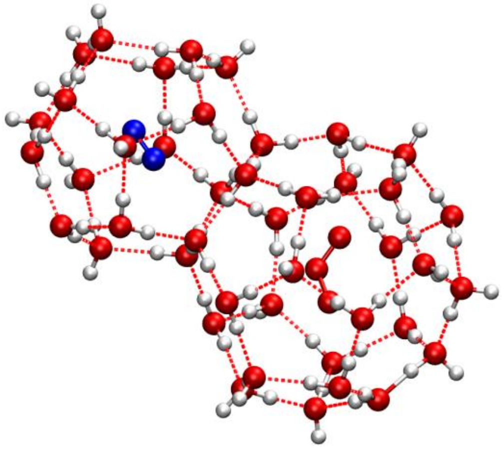
$O_2S + O_3L$ (**sI**)



$O_2S + O_3L$ (**sII**)



$N_2S + O_3L$ (**sI**)



$N_2S + O_3L$ (**sII**)

Vibration spectrum data

Frequencies of the guest molecule stretching vibrations are expressed in cm^{-1}. Obtained results are in agreement with the available experimental data for single and binary mixture hydrates (Table S4).

There are two sharp peaks caused by the Fermi resonance in CO_2 of the symmetric stretching mode (~1388 cm^{-1}) and the overtone of the bending mode (1285 cm^{-1}).[S2] In the hydrate form, the main CO_2 bands are still very pronounced and appear at ~1381 cm^{-1} and 1276.6 cm^{-1}.[S3] Due to this resonance, the calculated CO_2 values should be between the values for resonant vibrations.

Darling–Dennison resonance leads to the appearance of additional frequencies of intramolecular vibrations in O_3.[S4] Raman spectroscopy study revealed the peaks at 1036 cm^{-1} and 1106 cm^{-1}, which are pronounced[S5] and thus used for the comparison with calculated data.

N_2 and O_2 molecules are of a simplier structure, however, 2 peaks were experimentally found for both these gases in the hydrate form. Highest frequency peaks (1560 cm^{-1} for O_2 and 2335cm^{-1} for N_2)[S6] almost coincide with the free gas lines (1556 cm^{-1} for O_2 and 2331cm^{-1} for N_2)[S7]. However, later works showed that hydrate trapped N_2 stretched vibrations are shifted toward lower frequencies (~5 cm^{-1}) relative to that observed in the gas phase.[S3] It was suggested that appearance of the second N_2 and O_2 stretching peak could be caused by double cavity occupation, isotopic effect or different molecular environment of guest molecules (occupation of large and small cages)[S6]. All these cases are excluded in our calculations since we consider only single occupation of small cavity without any isotopic effect possibility, thus only one peak for both gases obtained.

Table S4 Raman mode of guest molecules (cm^{-1}) in vapor and hydrate phases.[a]

	Gas phase		in Hydrate			
			sI		**sII**	
Guest	Calc.	Exp	Calc	Exp	Calc	Exp
O_2 triplet	1540.24	1556[S7,S9]	1542.93		1541.8	1511,[S6] 1560[S6]
CO_2	1298.99	1285,[S7,S9] 1388[S7,S9]	1312.98	1277.8,[S10] 1380.7,[S10] 1276,[S11] 1381[S12]	1308.81	
N_2	2346.05	2331[S7,S9]	2352.03		2349.5	2291,[S6] 2335,[S6] 2324.5[S4]
O_3	1051.58, 1165.72	1036,[S5] 1106,[S5] 1042,[S12] 1103[S12]	1028.28, 1130.65		1040.85, 1134.56	
$O_2 + O_3$			O_2 : 1542.96 O_3 : 1038.94 O_3 : 1130.99		O_2 : 1536.80 O_3 : 1041.29 O_3 : 1135.40	O_2 : 1546[S13]
$CO_2 + O_3$			CO_2 : 1310.00 O_3 : 1042.58 O_3: 1130.71	CO_2 : 1274[S13] CO_2 : 1380[S13]	CO_2 : 1308.87 O_3 : 1039.38 O_3: 1134.59	
$N_2 + O_3$			N_2: 2351.39 O_3: 1037.29 O_3: 1136.99		N_2: 2349.02 O_3: 1040.68 O_3: 1134.70	N_2: 2322[S13]

[a] The frequency scalar factor of 0.9879 was selected.[S8]

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