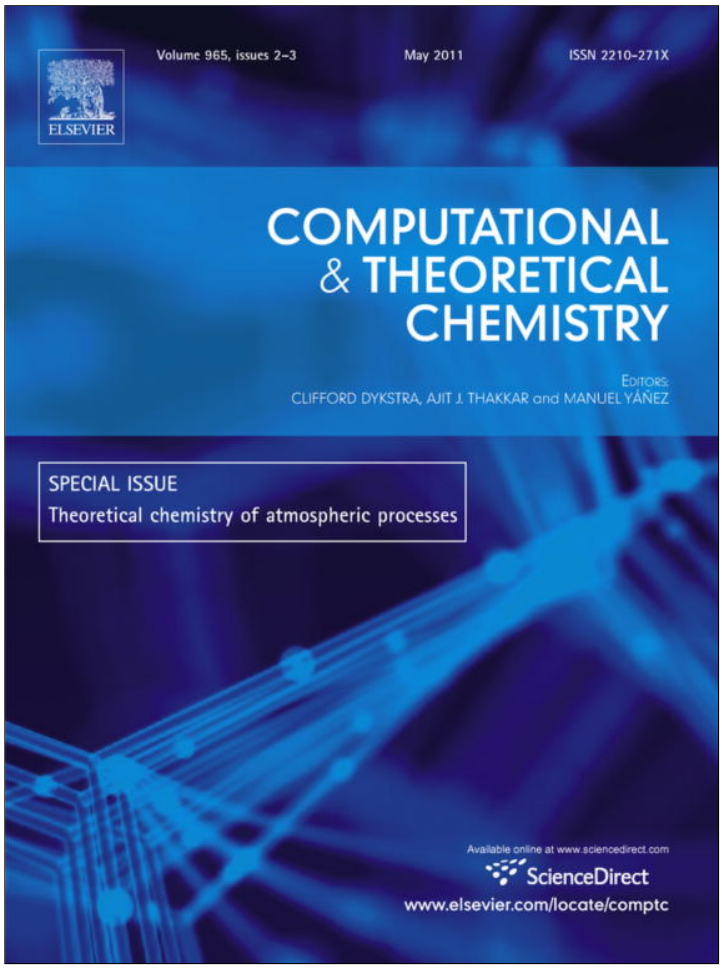

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Carbon dioxide–water clusters in the atmosphere of Mars

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ABSTRACT

The possibility of carbon dioxide–water binary nucleation in the atmosphere of Mars has been raised by some recent studies. We have studied the possible formation of mixed water–carbon dioxide clusters under Martian conditions using quantum mechanical calculations. We have performed these calculations for two different conditions relevant to the Martian atmosphere; high temperature and high water concentration, and low temperature and medium to low water concentration. In agreement with most observations, our results point to the formation of pure water clusters when the temperature and water concentration are high, and to the formation for pure carbon dioxide clusters when the temperature and water concentration are low. In the case of low temperature and medium water concentration, the stability of water clusters containing one carbon dioxide molecule is near the stability of pure clusters, so we cannot rule out the formation of these clusters in the Martian atmosphere under such specific conditions.

1. Introduction

Carbon dioxide (95.3%) and water (0.03% on average) are major volatiles compounds in the Martian atmosphere. Many studies have focused on the condensation of these compounds separately [1–9]. Only recent studies have raised the possibility of co-condensation/nucleation of these two compounds on the surface of Mars or in the Martian atmosphere [10–12].

The condensation of volatile compounds leads to the formation of polar ice caps on the surface of the planet in the winter, and to the formation of clouds in the atmosphere. Both water ice and carbon dioxide ice clouds have been observed [13–19]. Some studies have pointed out the possibility of CO_2–H_2O clathrate formation during the formation of the polar ice caps [10–11]. Ref. [10] studied this possibility with the help of a thermodynamical analysis of the CO_2–H_2O system phase equilibrium, whereas Ref. [11] performed kinetic experiments to evaluate the formation of clathrate on Mars and the effect of different parameters on it, as well as radiative transfer calculations to determine the detectability of CO_2 clathrate hydrate with spectroscopy. Clathrate formation on the surface of Mars raises the question of the possibility for mixed water–carbon dioxide clouds forming in the atmosphere as well, which was studied in detail by Ref. [12] with the help of a two-component nucleation model. Ref. [12] noted that the possibility of nucleation of these two components (CO_2 and H_2O) together cannot be ruled out, but that the uncertainties in the properties and the nature of the mixture (ideal/non-ideal) prevented Ref. [12] from drawing more definite conclusions.

In order to get a better insight in to this problem, we have decided to perform quantum mechanical calculations on different water–carbon dioxide clusters. Water clusters have been widely studied using quantum mechanical methods [20–22 and references therein]. On the other hand, carbon dioxide–water clusters have received less attention [22–23 and references therein]. As far as we know, there are no computational studies on pure carbon dioxide clusters in Martian conditions.

In the present study, we use a multi-step method, which has been successfully applied before to the study of different clusters relevant to the Earth's atmosphere [25–27], that combines density functional theory geometry and frequencies calculations, with coupled cluster single point energy calculation, to evaluate the possible formation of water–carbon dioxide mixed clusters (i.e. homogeneous binary nucleation). With that aim, we have computed the formation free energy of different water–carbon dioxide clusters, from pure ones (just water or carbon dioxide) to mixed clusters with different proportions of water and carbon dioxide, in different conditions found in Mars atmosphere.

2. Method

The applied multi-step method is described elsewhere [25] so only the relevant details are given here.

The initial guess geometries were chosen using chemical intuition and, when possible, geometries from earlier studies [20,24] (and references therein). The SPARTAN program [28] was then

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used to pre-optimize these structures. Once a large enough set of geometries was sampled, the more stable isomers (usually between 4 and 6) were optimized using the SIESTA program [29] using the gradient corrected BLYP functional [30] and the double-ζ polarized (DZP) basis set. Vibrational harmonic frequencies were also calculated using this program, and were used to estimate the entropy and thermal contributions to the enthalpy and Gibbs free energy of the clusters.

Finally, the optimized structures from the SIESTA program were used to perform single point energy calculations using the TURBOMOLE program [31] with the Resolution of Identity-Coupled Cluster Single and Doubles method (RI-CC2) [32]. The chosen basis set was aug-cc-pVTZ [33].

It should be noted that though the free energies computed using DFT are not quantitatively accurate for systems with large dispersion effects, such as carbon dioxide clusters, DFT – based geometries and frequencies combined with coupled-cluster energies can be used quite reliably for qualitative comparison, for example, different nucleation pathways (pure water or carbon dioxide versus mixed water–carbon dioxide clusters).

To obtain a realistic picture of the free energies in Martian atmospheric conditions, we have to take into account the relative concentration of each molecular species in the atmosphere of Mars. This is done via the law of mass action, with which the calculated free energies can be converted to ambient conditions using the partial pressures of each compound [25].

3. Results

Our main objective is to determine if clusters containing both water and carbon dioxide can be formed under different conditions in the Martian atmosphere. To achieve this, we have calculated the formation energies of clusters with different number of carbon dioxide and water molecules. For pure clusters (only water or carbon dioxide) we have calculated systems containing up to six molecules, $(CO_2)_n$ (n = 1–6),$(H_2O)_m$ (m = 1–6); for clusters with one water molecule we have calculated systems with up to six carbon dioxide molecules $(CO_2)_n{\cdot}(H_2O)$ (n = 1–6) and for clusters with one carbon dioxide molecule we have calculated systems up to four waters, $(CO_2)(H_2O)_m$ (m = 1–4). Finally, we have calculated data for clusters containing up to three waters and three carbon dioxide molecules,$(CO_2)_n(H_2O)_m$ (n = 1–3, m = 1–3). Fig. 1a shows the structure of most stable conformers for those clusters studied in this work that have, to our knowledge, not been computationally studied before (in practice, clusters with more than one carbon dioxide molecule), Fig. 1b shows the geometry parameters for some clusters, for clarity, only the smallest clusters from Fig. 1a were included.

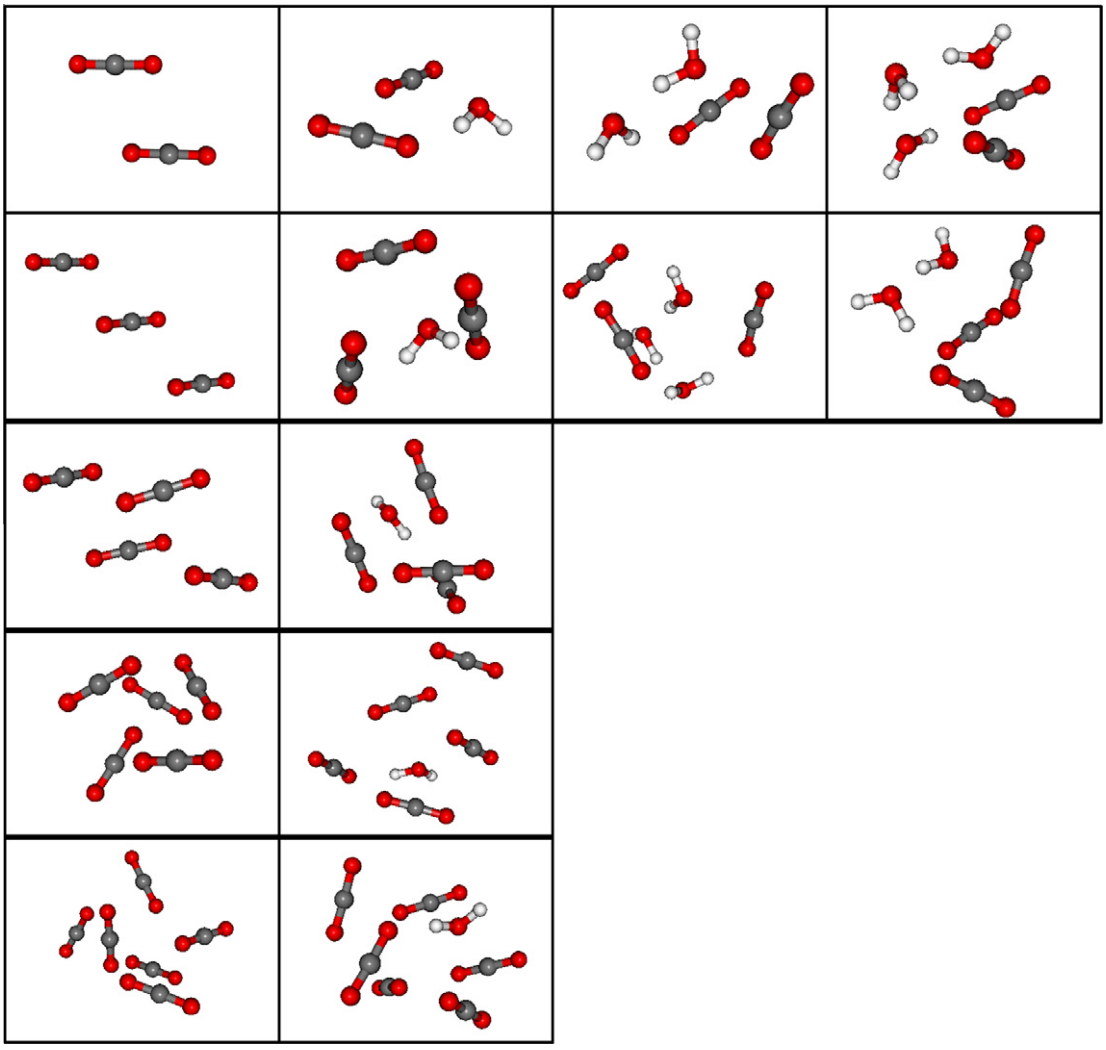

Fig. 1a. Most stable conformer structures for clusters containing more than one carbon dioxide molecule. Color coding: red, oxygen atom; black, carbon atom; white, hydrogen atom (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

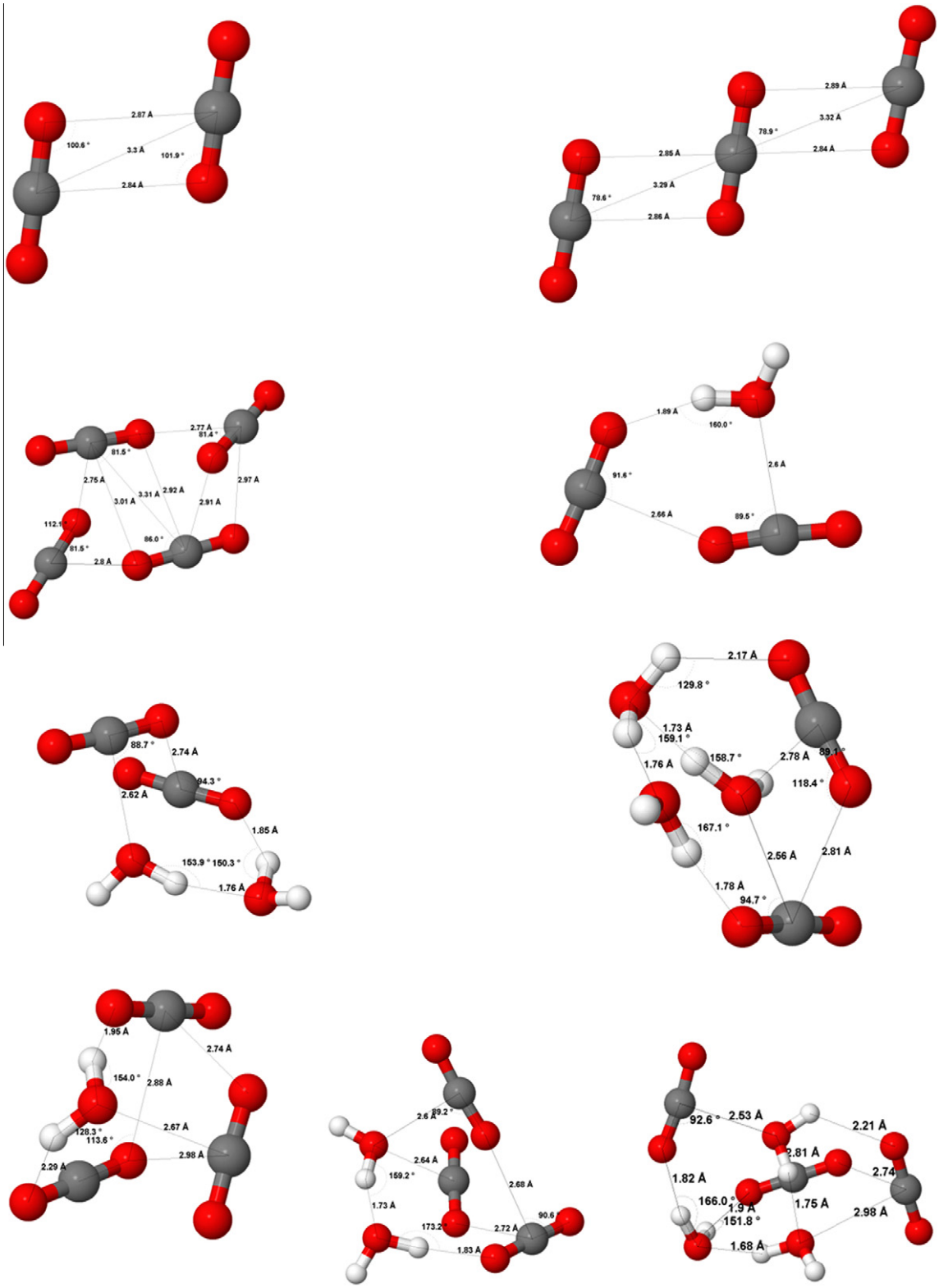

Fig. 1b. Geometry parameter for some of the clusters calculated. Color coding: red, oxygen atom; black, carbon atom; white, hydrogen atom (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 1 shows the Total electronic formation energies of different clusters (from monomers, for example, $nH_2O \rightarrow (H_2O)_n$).

Values for water clusters are in good agreement with previous high level studies (Dunn et al 2004). In order to evaluate the effect of the presence of water in the cluster we have calculated the incremental electronic energies of reaction $((CO_2)_{n-1} + CO_2 \rightarrow (CO_2)_n)$ (Table 2).

As we can see, the presence of one water molecule slightly enhances the addition of carbon dioxide to the clusters in all cases except for the addition of the fifth carbon dioxide molecule. In the

Table 1
Formation electronic energy from monomers of different water–carbon dioxide composition clusters in kcal/mol.

n CO_2	n H_2O	Formation electronic energy (kcal/mol)
2	0	−1.53
3	0	−3.09
4	0	−6.15
5	0	−10.75
6	0	−14.49
1	1	−2.38
1	2	−9.09
1	3	−16.73
1	4	−30.41
2	1	−5.62
2	2	−13.61
2	3	−22.82
3	1	−9.33
3	2	−18.01
3	3	−26.09
4	1	−13.74
5	1	−16.62
6	1	−24.20
0	2	−4.74
0	3	−14.98
0	4	−25.93
0	5	−35.32
0	6	−45.12

Table 2
Incremental electronic energies for addition of a carbon dioxide molecule to the cluster (kcal/mol).

$(CO_2)_{n-1} + CO_2 \rightarrow (CO_2)_n$	Water molecules in the cluster			
n	0	1	2	3
2	−1.53	−3.24	−4.51	−6.09
3	−1.56	−3.71	−4.40	−3.28
4	−3.06	−4.42		
5	−4.60	−2.88		
6	−3.74	−7.58		

Table 3
Formation free energy in kcal/mol for clusters with different compositions at 180 K and a water partial pressure of 18 Pa.

Cluster composition	Total number of molecules in the cluster					
	2	3	4	5	6	7
CO_2	7.89	15.87	23.32	29.05	36.74	
H_2O	9.54	12.53	13.95	17.29	21.47	
$CO_2{\cdot}(H_2O)_n$	9.10	15.40	19.67	20.50		
$H_2O{\cdot}(CO_2)_n$	9.10	16.10	21.66	29.42	36.20	39.70
1:1 CO_2:H_2O	9.10		21.50		32.95	

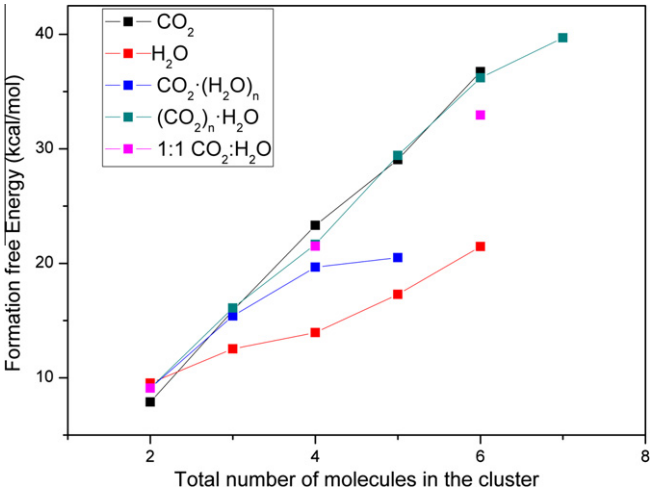

Fig. 2. Formation free energy at 180 K and 0.03% water fraction (18 Pa) versus total number of molecules. Black solid line: pure carbon dioxide clusters; red solid line: pure water clusters; blue solid line: water cluster with one carbon dioxide molecule; green solid line: carbon dioxide cluster with one water molecule, magenta points: clusters with 1:1 water–carbon dioxide proportion. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4
Formation free energy in kcal/mol for cluster with different compositions at 100 K and: (a) 1 ppm, (b) 1 ppb (c) 1 ppt water partial pressures.

Cluster composition	Total number of molecules in the cluster					
	2	3	4	5	6	7
(a)						
CO_2	3.62	*7.50*	10.42	11.80	14.73	
H_2O	6.49	5.85	3.80	3.57	3.89	
$CO_2{\cdot}(H_2O)_n$	5.49	8.13	9.09	8.69		
$H_2O{\cdot}(CO_2)_n$	10.99	16.52	*20.67*	26.29	31.60	33.22
1:1 CO_2:H_2O	5.49		9.85		13.23	
(b)						
CO_2	3.62	*7.50*	10.42	11.80	14.73	
H_2O	9.22	9.95	9.26	10.39	12.07	
$CO_2{\cdot}(H_2O)_n$	6.86	10.88	13.21	11.44		
$H_2O{\cdot}(CO_2)_n$	12.36	19.27	*24.79*	31.78	38.46	41.45
1:1 CO_2:H_2O	6.86		12.59		17.35	
(c)						
CO_2	3.62	*7.50*	10.42	11.80	14.73	
H_2O	11.97	14.06	14.75	17.26	20.31	
$CO_2{\cdot}(H_2O)_n$	8.24	13.62	17.32	16.93		
$H_2O{\cdot}(CO_2)_n$	13.74	22.01	*28.91*	37.27	45.32	49.69
1:1 CO_2:H_2O	8.24		15.34		21.46	

case of the cluster with two water molecules, we can observe the same phenomenon. For clusters with three water molecules, the addition of the third carbon dioxide molecule is more favorable compared to unhydrated carbon dioxide clusters, but less favorable that for mono and di-hydrated clusters.

Electronic energies can give us some idea of the interaction energies of these molecules, but to get a better description of these clusters in the Martian atmosphere, we need to compute Gibbs free energies using the conditions of Mars. The cluster formation free energy depends on the relative atmospheric concentration of each molecular species in the atmosphere trough the law of mass action as shown by Ortega et al. [25]. Note that the absolute values of the presented formation free energies are arbitrary, as the concentration of the product clusters in the formation reactions are set to Martian reference pressure (600 Pa), and only the monomer concentrations are varied. The relative values of the formation free energies, on the other hand, allow a realistic comparison of the stabilities of the different clusters.

We have considered 95% (570 Pa) for carbon dioxide concentration and values between 300 ppm and 1 ppt ($18–6 \times 10^{-8}$ Pa) for water. [34]. For simplicity, we have omitted the decrease in total pressure with altitude, since this does not affect the comparison of formation energies between different clusters; only the relative concentration of carbon dioxide and water are relevant in this context.

3.1. High temperature and high water concentration

For this scenario we have chosen a temperature of 180 K and a water partial pressure of 18 Pa. (equal to 300 ppm given a total Martian atmospheric pressure of 600 Pa.).

Table 3 shows the formation free energies for different clusters under these conditions, and Fig. 2 shows formation free energy of different clusters versus total number of molecules in the cluster.

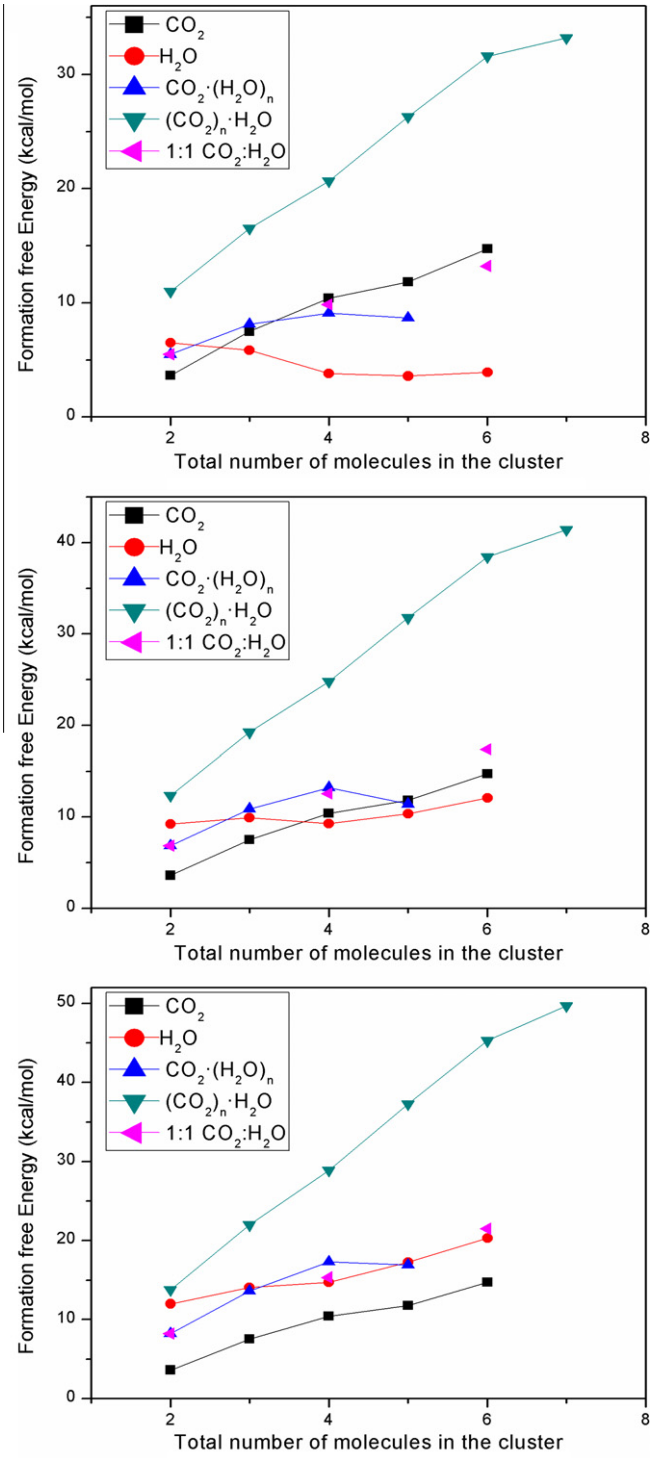

Fig. 3. Formation free energy at 100 K and: upper panel: 1 ppm, middle panel: 1 ppb, bottom panel: 1 ppb water fractions versus total number of molecules. Black solid line: pure carbon dioxide clusters; red solid line: pure water clusters; blue solid line: water cluster with one carbon dioxide molecule; green solid line: carbon dioxide cluster with one water molecule; magenta points: Clusters with 1:1 water–carbon dioxide proportion. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As we can see, in these conditions the formation of pure water clusters is the most favorable process, while formation of pure carbon dioxide cluster is less favorable. The presence of water in the cluster does not help the cluster to grow. These results point to the formation of only pure water clusters under these conditions. This conclusion agrees with the observation of pure water clouds near the Martian surface. Note that the true cloud-forming processes are likely to involve other mechanisms than pure homogeneous water nucleation, such as heterogeneous nucleation on dust particles.

3.2. Low temperature and medium–low water concentration

For this scenario we have calculated formation free energy of the carbon dioxide–water clusters at 100 K and using water partial pressures from 6×10^{-2} Pa to 6×10^{-8} Pa (1 ppm–1 ppt).

The results are summarized in Table 4a–c.

In Fig. 3 we present the formation free energy of clusters at different water concentrations.

For a water fraction of 1 ppm (6×10^{-2} Pa), the formation of pure water cluster is most favorable. For the clusters containing six molecules, the energy difference is around 11 kcal/mol between pure carbon dioxide and pure water clusters. If we lower the water partial pressure to 1 ppb (6×10^{-5} Pa), pure carbon dioxide clusters start to be more stable than pure water clusters at small sizes, but then again large water cluster are more stable. This time, the energy difference between the pure six molecule clusters is rather small (2.7 kcal/mol). The formation free energies of clusters containing only one molecule of carbon dioxide are closer to that of pure water and pure carbon dioxide (for five molecules clusters all energies are within 1.5 kcal/mol of each other).

When the water fraction drops to 1 ppt, pure carbon dioxide clusters become the most stable ones, with on average 5.90 kcal/mol lower formation free energies than for pure water or mixed clusters.

Thus, when the water fraction is above 1 ppb, pure water clusters will be far more stable than carbon dioxide or mixed clusters. If the concentration is lower, the pure carbon dioxide cluster will dominate. We can also see how even with a 1 ppb water concentration, the only mixed clusters that have formation free energies close to pure clusters are those containing only one carbon dioxide molecule.

4. Conclusions

We have carried out quantum mechanical calculations on carbon dioxide–water clusters of different composition, and under different conditions similar to those found on Mars, to evaluate the existence of mixed water–carbon dioxide clusters.

Our calculations indicate that at high temperatures and high water concentrations, the formation of pure water clusters is preferred over the formation of mixed or pure carbon dioxide clusters. These kinds of conditions prevail in the lowest part of the Martian atmosphere, and these results are in good agreement with the observed formation of water ice clouds on Mars.

In the case of low temperature, the dominating clusters will depend on the water concentration. For a 1 ppm water fraction, water clusters will clearly dominate, while for a 1 ppt water fraction, carbon dioxide clusters will be the dominating ones. With a 1 ppb water fraction, the most stable clusters are large water clusters, but the energy difference between pure carbon dioxide and water–carbon dioxide clusters is rather small. The results agree with the observation of pure carbon dioxide clouds at high altitudes, where the concentration of water is low. The formation of small mixed clusters with more than one carbon dioxide molecule seem unlikely, but we cannot completely rule out the formation, under some specific conditions, of small water clusters containing one carbon dioxide molecule.

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