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Water clustering in the presence of a CO_2 molecule

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ABSTRACT

The gas-phase geometries of the complexes CW*n* formed between one CO_2 molecule and various numbers n of water molecules (n = 1–8) have been examined using the Møller–Plesset perturbation (MP2) and the density functional methods coupled with the aug-cc-pVDZ basis set. For a given number of water molecules, the latter aggregate in a stable complex with strong hydrogen bonds on one side of the CO_2 molecule. The reported stabilization energies associated with the clustering of CO_2 and water molecules have been corrected for the basis set superposition error. van der Waals and O—H···O_C interactions bind the water and CO_2 molecules in the complexes. It was also found that the water moieties of some of the optimized structures of the CW4—CW8 complexes resemble the water moieties of the well known gas hydrates. The Gibbs free energy changes for clustering of molecules as stable complexes were calculated at various temperatures. These calculations revealed that their formation is spontaneous at sufficiently low temperatures. The stretching frequency of the CO_2 in the complex increases and that of the water molecules attached to the CO_2 molecule decreases compared to their free states. These shifts depend on the strength of the O—H···O_C interaction. The comparison between the stabilization energies of a number of complexes $CO_2(H_2O)_n$, indicated that their stabilization energies are approximately equal to the sum of the stabilization energies of two moieties of $CO_2(H_2O)_{n/2}$ provided that their $(H_2O)_{n/2}$ are located on the opposite sides of CO_2.

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1. Introduction

The hydration of CO_2 is an important reaction, both in biological and environmental processes. It is well known that the formation of carbonic acid from CO_2 and water plays an important role in controlling the pH of blood [1]. The crucial role of CO_2 in the global warming, suggested its sequestration via CO_2 hydrate formation [2]. Whereas the lone electron pair of the oxygen atoms of CO_2 makes the molecule partially hydrophilic, the much smaller electronegativity of the carbon atom makes the molecule partially hydrophobic. Being a small molecule with two different types of sites, CO_2 can serve as a candidate for the study of solvation. The clusters which are formed between CO_2 and water molecules, $CO_2(H_2O)_n$ (hereafter referred to as CW*n* clusters), can be considered as model compounds for the examination of the molecular interactions in aqueous solutions.

Regarding the hydration of CO_2, numerous investigations have been carried out, both experimentally and theoretically [3–18]. The formation of weak van der Waals complexes CW1 and CW2 has been identified by Peterson and his group from molecular beam studies [4,5]. Columberg et al. have reported the microwave spectrum of the complex CW1 [6]. Using supersonic jet expansions followed by the synchrotron ionization technique, Shimoru et al. have studied the clusters CW1 and CW2 [7]. Recently, Schriver et al. [8] have reported the Fourier transform infrared (FTIR) spectra of CW1 complexes. From ab initio and free energy perturbation simulations, Merz concluded that the reaction of CO_2 with two water molecules is more favorable than that with one water molecule [10]. By incorporating up to four water molecules and using ab initio calculations and various continuum solvation models, Nguyen et al. [12,17] found that the solvent (water) does not act only as a reaction medium but is also actively involved in the hydration of CO_2. The catalytic role of the solvent molecules in the hydration of CO_2 has been also examined by Lewis and Glaser and compared with the hydration of $C(NH)_2$. They found that the catalytic effect of the solvent increases with the polarizability of the heteroatom which is larger for N than O [13].

Attempts have been also made to examine the structure and stability of complexes formed between a CO_2 molecule and various numbers of water molecules. For example, Merz has examined the complexes of CO_2 with one and two water molecules using the Møller–Plesset perturbation methods and various basis sets [10]. Lewis and Glaser have carried out calculations up to three water molecules [13]. Using the MP2 method and the aug-cc-pVTZ basis set, Nguyen et al. carried out calculations up to four water molecules with particular emphasis on the formation of the carbonic acid [9,12,17]. Jena and Mishra have performed density functional

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calculations using the B3LYP parametrization and aug-cc-pVDZ basis set for CW*n* clusters up to eight water molecules [14]. They have compared the geometries obtained via B3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ for CW1 clusters and found that the geometry obtained via B3LYP/aug-cc-pVDZ has a planar symmetric structure, whereas the latter MP2 calculation provides a planar asymmetric structure. Using the nitrogen matrix isolation technique, Schriver et al. have recorded the FTIR spectra of the two complexes of CW1 [8]. Recently, the complex potential energy surface of CW1 was examined by Makarewicz, who pointed out that the MP2 method, in which the correlation energy plays an important role, describes adequately this system [18]. Keeping this in mind and considering the inefficiency of the B3LYP method in representing the weak interactions [19–21], we have carried out extensive calculations using the MP2 method and the aug-cc-pVDZ basis set for CW*n* clusters with up to eight water molecules. The Gibbs free energy change (ΔG) associated with the clustering of water molecules in the presence of CO_2 was also calculated for all stable complexes of CO_2 $(H_2O)_n$.

2. Computational details

All the calculations of the present paper were carried out by using the program GAMESS on Dell Linux machines coupled to 64 bit Xeon processors [22]. The optimizations were performed using the second order Møller–Plesset Perturbation method (MP2) and the aug-cc-pVDZ basis set. The convergence tolerance of the gradient used for optimization was 10^{-6} Hartree/Bohr. The linear combination of the basis functions was constructed using the spherical harmonic functions as available in the program. Vibrational frequency calculations were carried out to distinguish between minima and saddle points. For a given number of water molecules, the complex with the lowest energy, which constitutes also a minimum in the potential energy surface was identified as the stable complex. The other minima of the corresponding potential energy surface obtained are metastable complexes.

The stabilization energies of the optimized geometries were calculated using the supermolecular approach and the results have been corrected for the basis set superposition error using the counterpoise method [23]. The zero point energy corrections were included in the stabilization energies of the stable complexes. The results obtained are listed in Table 1. Single point energy calculations with the appropriate density functionals M05-2X, M06 and M06-2X and the aug-cc-pVDZ basis set have been also carried out for the stable complexes using their MP2/aug-cc-pVDZ optimized geometries. These density functionals have been reported to be suitable for systems in which non-covalent interactions are present [24]. The Gibbs free energy change associated with the formation of stable complexes was calculated with respect to the isolated CO_2 and water molecules. By considering the effect of temperature on the partition functions and the associated changes of the thermodynamic quantities, the Gibbs free energy change for clustering at different temperatures were calculated using the procedure available in the program. The results are discussed below.

3. Results and discussion

The optimized geometries of the CW*n* clusters are presented in Fig. 1. The complex **CW1a** is formed between one CO_2 and one water molecules. In this complex, one of the O—H bonds of the water molecules is almost parallel to one of the C=O bonds. The complex is planar and unsymmetric, in agreement with some of the earlier experimental and theoretical studies [8,14,15]. The calculated stabilization energy of **CW1a** is −2.99 kcal/mol. By including the basis set superposition error (BSSE) and the zero point energy (ZPE) corrections, the complex was found to remain stable with a stabilization energy of −1.36 kcal/mol.

Table 1
Calculated stabilization energies and relevant distances between various atoms for the CW*n* clusters with n = 1–8, at the MP2/aug-cc-pVDZ level.

CW*n*	Symbol	Stabilization energy (kcal/mol) MP2/aug-cc-pVDZ		O—H···O_C distance (Å)	C···O_W distance (Å)
		With BSSE correction	With BSSE and ZPE correction		
CW1	**CW1a**	**−2.26**	**−1.36**	**–**	2.784
	CW1b	−1.44		–	2.936
	CW1c	−0.08		2.829	3.396
CW2	**CW2a**	**−8.52**	**−5.39**	2.146	2.766
	CW2b	−3.95		2.608	2.869
CW3	**CW3a**	**−16.79**	**−10.39**	2.581	2.945
	CW3b	−13.19		2.226	2.711
	CW3c	−12.57		2.136	2.700
CW4	**CW4a**	**−27.10**	**−17.85**	2.591	3.139
	CW4b	−25.99		2.558	3.024
	CW4c	−22.41		2.206	2.776
	CW4d	−16.99		2.122	2.821
CW5	**CW5a**	**−35.18**	**−23.68**	2.496	2.882
CW6	**CW6a**	**−43.63**	**−29.26**	2.386	2.865
	CW6b	−43.47		2.538	2.881
	CW6c	−42.84		2.409	2.942
	CW6d	−32.88		2.500	2.987
	CW6e	−25.40		2.229	2.757
CW7	**CW7a**	**−53.94**	**−36.38**	2.065	2.908
	CW7b	−52.37		2.495	2.899
	CW7c	−52.23		2.298	2.830
CW8	**CW8a**	**−66.61**	**−45.05**	2.715	2.876
	CW8b	−64.22		3.477	2.918
	CW8c	−61.74		1.966	2.817
	CW8d	−59.19		2.300	2.893
	CW8e	−53.74		2.570	3.192

In addition to the orientation of the water molecule as in **CW1a**, the water molecule can orient in a variety of ways. Among the different orientations of the water molecule around CO_2, the optimized complexes **CW1b** and **CW1c** are noteworthy. Whereas the hydrogen atoms of H_2O are directed away from the CO_2 molecule in **CW1b**, they are directed towards the oxygen atoms of CO_2 in **CW1c.** Frequency calculations indicated that both structures correspond to second order saddle points on the potential energy surface. Examination of the energies of these complexes indicated that they are unstable with respect to **CW1a,** but, stable with respect to the isolated water and CO_2 molecules.

The lower stabilization energies of **CW1b** and **CW1c** when compared to that of **CW1a** (see Table 1) can be correlated with the Mulliken charges on the carbon atom of CO_2 and on the oxygen atom of H_2O. For **CW1a**, the Mulliken charges of the atoms mentioned above are 0.4062 and −0.2982, respectively. For **CW1b** and **CW1c** the corresponding charges are 0.3758 and −0.2859 and 0.3476 and −0.2595, respectively. Large differences in charges provide stronger attractive interactions between the carbon of CO_2 and the oxygen of water. The difference in stabilization energies for the above three complexes can also be related to the distance between the carbon atom of CO_2 and the oxygen atom of water. The C···O_W distances for **CW1a**, **CW1b** and **CW1c** are 2.784 Å, 2.936 Å and 3.396 Å, respectively. Thus, the longer the distance between the two atoms, the lower (less negative) is the stabilization energy because of less interaction between them. It is worth mentioning that the experimentally obtained C···O_W distance is 2.836 Å [4], hence close to that of **CW1a**.

One should emphasize that unlike the interaction between the protonated water with CO_2, no hydrogen bond is formed between