

Research Article

Theoretical Investigation of the Cooperativity in $\text{CH}_3\text{CHO}\cdot 2\text{H}_2\text{O}$, $\text{CH}_2\text{FCHO}\cdot 2\text{H}_2\text{O}$, and $\text{CH}_3\text{CFO}\cdot 2\text{H}_2\text{O}$ Systems

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The hydrogen bond interaction between CH_3CHO , CH_2FCHO , and CH_3CFO and two water molecules is investigated at the B3LYP/6-311++G(d,p) level. The results are compared with the complexes involving the same carbonyl derivatives and one water molecule. The calculations involve the optimization of the structure, the harmonic vibrational frequencies, and relevant NBO (natural bond orbital) parameters such as the NBO charges, the occupation of antibonding orbitals, and intra- and intermolecular hyperconjugation energies. Two stable cyclic structures are predicted. The two structures are stabilized by $\text{C}=\text{O}\cdots\text{HO}$ hydrogen bond. The A structures are further stabilized by $\text{CH}\cdots\text{O}$ bond involving the CH_3 (CH_2F) group. This bond results in an elongation of the CH bond and red shift of the $\nu(\text{CH})$ vibration. The B structures are stabilized by $\text{CH}\cdots\text{O}$ interaction involving the aldehydic CH bond. The formation of this bond results in a marked contraction of the CH bond and blue shift of the $\nu(\text{CH})$ vibration indicating the predominance of the lone pair effect in determining the CH distances. The total interaction energies range from -12.40 to -13.50 kcal mol^{-1} . The cooperative energies calculated at the trimer geometry are comprised between -2.30 and -2.60 kcal mol^{-1} .

1. Introduction

Cooperative interactions involving three or more molecules are an important component of intermolecular interactions, particularly those involving hydrogen bonds. The cooperativity of hydrogen bonds plays an important role in controlling and regulating the processes in living materials. This has been recognized since a long time and quantitative aspects of cooperativity have been discussed [1–7]. Cooperativity can be positive or negative. It has been shown that a first hydrogen bond involving a given site of a molecule weakens the reactivity of the neighboring sites of the same nature whereas it enhances the electron donor power of the adjacent sites of opposite nature [4]. Cooperativity between water molecules is particularly important, because in liquid water at room temperature, the great majority of the molecules are hydrogen-bonded to each other, the concentration of “free” OH groups being very low [8]. For this reason, extensive theoretical calculations have been carried out on

the cooperativity in water [9–13]. In recent works, the interaction between proton acceptors (or donors) and two (or more) water molecules has been discussed [14–21].

In a recent work [22], the complexes between acetaldehyde and some of its monofluorinated derivatives and one water molecule have been investigated by theoretical methods. It was shown in this work that water acts as a proton donor toward the $\text{C}=\text{O}$ bond forming $\text{C}=\text{O}\cdots\text{HO}$ hydrogen bonds but that water can also act as a proton acceptor forming weak $\text{CH}\cdots\text{O}$ hydrogen bonds. It seemed to us interesting to investigate the interaction between some of these carbonyl derivatives (CH_3CHO , CH_2FCHO , and CH_3CFO) and two water molecules in order to discuss the effect of cooperativity in these hydrogen-bonded systems. To the best of our knowledge, no experimental data are available for these systems.

This paper is arranged as follows. The first step of our study deals with the structure of the complexes. In the second section, the intramolecular distances, some

vibrational frequencies and the results of a natural bond orbital (NBO) analysis are discussed. A special attention is paid to the NBO charges, occupation of antibonding orbitals, and hyperconjugation energies. In the last section, the cooperative energies are discussed.

2. Computational Methods

Calculations of the properties of CH_3CHO , CH_2FCHO , and CH_3CFO , complexed with two water molecules were carried out using the density functional B3LYP method [23] and the Gaussian suite of programs [24]. The basis set 6-311++G(d, p) was invoked. The second-order Møller-Plesset MP2/aug-cc-PVTZ method was also used to calculate some of the structures or binding energies. The computed interaction energies were corrected for the basis superposition error (BSSE) [25].

The cooperativity in a molecular trimer containing A, B, and C molecules is given by the three-body term ΔE_{coop} which can be defined as the difference between the total interaction energy $E_{\text{int}}(\text{ABC})$ and the sum of the pairwise or two-body interaction energies $E_2(\text{AB})$, $E_2(\text{BC})$, $E_2(\text{AC})$.

$$\Delta E_{\text{coop}} = E_{\text{int}}(\text{ABC}) - E_2(\text{AB}) - E_2(\text{BC}) - E_2(\text{AC}). \quad (1)$$

Here, the E_2 values correspond to the two-body contributions at the trimer geometry [26–28] calculated with the same basis set.

The harmonic vibrational frequencies were calculated to characterize the stationary points. No scaling factor was used. The charges on individual atoms, orbital occupancies, and hyperconjugation energies were obtained by an NBO analysis [29].

3. Results and Discussion

3.1. Structure of the Complexes between CH_3CHO , CH_2FCHO , and CH_3CFO with Two Water Molecules. Figure 1 illustrates the structure of the 1-2 complexes between CH_3CHO , CH_2CHO , and CH_3CFO with two water molecules calculated with the B3LYP functional. The distances calculated with the MP2 method are somewhat shorter. The structure of the complexes with one water molecule taken from a previous work [22] is shown for the comparison. As shown in this work, the 1-1 complexes are characterized by two stable structures. In both A and B structures, the molecules are held together by a $\text{C}=\text{O} \cdots \text{HO}$ hydrogen bond. The A complexes are cyclic and stabilized by a weak $\text{C}_4\text{H}_5 \cdots \text{O}$ interaction and they are slightly more stable than the B complexes. These structures have been established by considering the intermolecular $\text{H}_5 \cdots \text{O}$ distances and some NBO parameters such as the weak intermolecular charge transfer from the O atom of water to the $\sigma^*(\text{C}_4\text{H}_5)$ orbital. In none of the 1-1 complexes the C_1H_3 bond was involved in the formation of a cyclic structure. Let us notice that CH_3CFO is also able to form a cyclic complex with two water molecules, one of the OH bonds of the water dimer being bonded to the F atom. This complex will not be considered here.

In none of the 1-2 complexes the second water molecule is bonded to the second electron pair of the carbonyl O atom. This structure is anticooperative, both electron donor sites having the same nature [4]. As shown in Figure 1, the intermolecular $\text{C}=\text{O} \cdots \text{HO}$ distances are shortened with respect to their values in the 1-1 complexes by amounts ranging from 0.081 to 0.109 Å. Further, the $\text{O}_9 \cdots \text{H}_{11}$ distances ranging from 1.840 to 1.866 Å are shorter than in the water dimer (1.933 Å). The most spectacular indication of a positive cooperativity is the shortening of the $\text{H}_5 \cdots \text{O}$ distances by 0.212 Å in CH_3CHO (A1-2), 0.585 Å in CH_2FCHO (A1-2), and 0.194 Å in CH_3CFO (A1-2). The short $\text{H}_3 \cdots \text{O}$ distances of 2.319 Å in CH_3CHO (B1-2), and 2.255 Å in CH_2FCHO (B1-2) also indicates that the trimer is stabilized by a $\text{C}_1\text{H}_3 \cdots \text{O}$ interaction. This will be further confirmed by the NBO data. Therefore, the hydrogen bond pattern appears to be different in the B(1-1) and B(1-2) complexes. We note also an increase in the angles, the $\text{C}_4\text{H}_5 \cdots \text{O}$ bond becoming almost linear in both A(1-2) complexes involving CH_3CHO and CH_3CFO and increasing by 40–50° in the other structures. The $\text{OH} \cdots \text{O}$ angles decrease by 10 to 17° from its value in the water dimer (175°).

3.2. Geometrical and NBO Properties of the Complexes. Tables 1, 2, and 3 list some relevant geometrical properties of the complexes, namely the C_1H_3 , C_4H_5 , $\text{C}=\text{O}$, and HO distances in the isolated monomers, in the 1-1 and in the 1-2 complexes with water. The corresponding vibrational frequencies are indicated as well. Tables 1, 2, and 3 also indicate important NBO parameters, namely, the occupation of $\sigma^*(\text{C}_1\text{H}_3)$ or $\sigma^*(\text{C}_4\text{H}_5)$ antibonding orbitals, the NBO charges along with some intra- or intermolecular hyperconjugative interactions.

Inspection of the results of Tables 1, 2, and 3 shows that the elongation of the $\text{C}=\text{O}$ bonds and the decrease of the $\nu(\text{C}=\text{O})$ vibrational frequencies are larger for the 1-2 than for the 1-1 complexes. Both parameters are linearly related [30] and suggest a reinforcement of the $\text{C}=\text{O} \cdots \text{HO}$ interaction in the 1-2 complexes. These data will no more be discussed hereafter, the main scope of this section being the discussion of the properties of the CH bonds.

Let us at first discuss the properties of the C_1H_3 bond in the CH_3CHO and CH_2FCHO complexes. As discussed in [22], the contraction of the C_1H_3 bond and the increase of the corresponding vibrational $\nu(\text{C}_1\text{H}_3)$ frequencies in the A(1-1) and B(1-1) complexes results from the classical lone pair effect [31–40]. The C_1H_3 distances, the $\sigma^*(\text{C}_1\text{H}_3)$ occupation and the intramolecular $\text{LPO}_2 \rightarrow \sigma^*(\text{C}_1\text{H}_3)$ hyperconjugation energies are almost identical in the A(1-1) and A(1-2) complexes. The intramolecular hyperconjugation energies decrease by 1.42 kcal mol⁻¹ (CH_3CHO (1-2)) and by 1.61 kcal mol⁻¹ (CH_2FCHO (1-2)) from the isolated molecules. As discussed in the first section, the short intermolecular $\text{H}_3 \cdots \text{O}$ distances suggest that the C_1H_3 bond is involved in the formation of the cyclic structure in the two B(1-2) complexes. This is in full agreement with the relatively large intermolecular charge transfer from the O_{12} atom of water to the $\sigma^*(\text{C}_1\text{H}_3)$ orbital (2.70 and

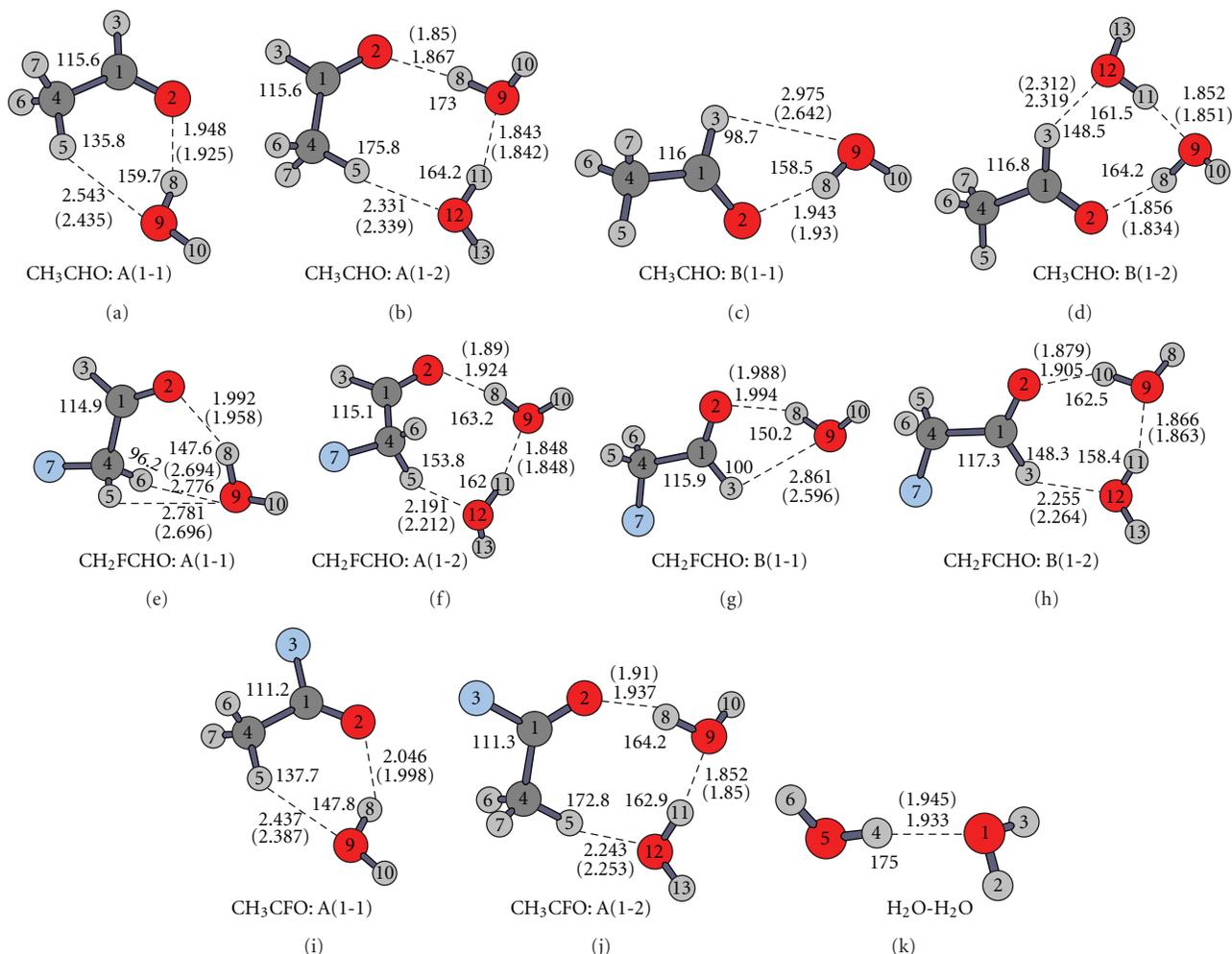


FIGURE 1: A and B structures of CH_3CHO , CH_2FCHO , and CH_3CFO complexed with one and two water molecules calculated at B3LYP/6-311++G(d,p) level. The distances calculated with the MP2/aug-cc-PVTZ method are indicated in parentheses.

$3.40 \text{ kcal mol}^{-1}$). Despite this charge transfer, the $\sigma^*(\text{C}_1\text{H}_3)$ occupation decreases. This can be explained by the large variation of the $\text{LPO}_2\sigma^*(\text{C}_1\text{H}_3)$ hyperconjugation which decreases by $4.8 \text{ kcal mol}^{-1}$ in both B(1-2) complexes. This illustrates the predominance of the lone pair effect in determining the C_1H_3 distances. These distances are linearly related to the $\sigma^*(\text{C}_1\text{H}_3)$ occupation as follows:

$$r(\text{C}_1\text{H}_3)(\text{\AA}) = 0.448 \sigma^*(\text{C}_1\text{H}_3)(e) + 1.0801 \quad (r = 0.961). \quad (2)$$

The small increase of the s-character of the $\text{C}_1(\text{H}_3)$ atom in the B(1-2) complexes does not influence the C_1H_3 distances to a great extent.

Parallel to the decrease of the C_1H_3 distances, the large blue shift of the $\nu(\text{C}_1\text{H}_3)$ vibration must be noticed (93 cm^{-1} and 61 cm^{-1}). Let us notice that the blue shift of 93 cm^{-1} in the CH_3CHO (B1-2) system is one of the largest ones predicted in $\text{CH} \cdots \text{O}$ hydrogen bonds involving neutral molecules [41–48]. In the present cases, the cooperativity results in an increase of the blue shift. This increase has also been found for other systems. For $\text{H}_2\text{C}=\text{O}$ complexed with

one and two water molecules, the blue shifts of the $\nu^s(\text{CH})$ vibration are 45 and 66 cm^{-1} , respectively, [17]. For CH_3Cl complexed with one and two water molecules, the blue shifts are 13 and 25 cm^{-1} , respectively [19]. Further, the increase of the polarity of the C_1H_3 bond in the B(1-2) complexes is also worth noticing, the positive charge on the proton being about $0.06e$ larger than in the isolated molecules.

In a next step, we will discuss the properties of the C_4H_5 bond in the three carbonyl complexes. As shown in our previous study [22], the C_4H_5 bonds in the CH_3 or CH_2F groups are weakly sensitive to the formation of a hydrogen bond with the O atom of water. In the acetone- H_2O complex as, for example, the two CH bonds which do not participate in the interaction show a greater sensitivity to hydrogen bond formation than the CH bond involved in the interaction. This was rather unexpected and was explained by the orbital interaction between the bonding $\sigma(\text{CH})$ orbital and the antibonding $\sigma^*(\text{C}=\text{O})$ and $\pi^*(\text{C}=\text{O})$ orbitals [22]. For the 1-2 complexes considered here, the value of this interaction remains almost constant. For the C_4H_5 bond of CH_3CHO , the value of this orbital interaction is equal

TABLE 1: Properties of the isolated CH₃CHO and H₂O molecules, A and B complexed with 1 and 2 water molecules (distances in Å, σ^* occupation in e, hyperconjugation energies in kcal mol⁻¹, and frequencies in cm⁻¹).

	Isolated CH ₃ CHO	A(1-1)	A(1-2)	B(1-1)	B(1-2)
$r(\text{C}_1\text{H}_3)$	1.1122	1.1094	1.1094	1.1082	1.1054
$\nu(\text{C}_1\text{H}_3)$	2871	2905	2906	2923	2964
$\sigma^*(\text{C}_1\text{H}_3)$	0.071	0.064	0.063	0.062	0.057
%sC ₁ (H ₃)	30.0	30.0	29.7	30.0	31.7
$q(\text{C}_1)$	0.442	0.463	0.474	0.457	0.451
$q(\text{H}_3)$	0.092	0.103	0.103	0.116	0.153
$r(\text{C}_4\text{H}_5)$	1.0898	1.0897	1.0910	1.0896	1.0898
$\nu(\text{C}_4\text{H}_5)$	3136	3142	3125	3139	3136
$\sigma^*(\text{C}_4\text{H}_5)$	0.0066	0.0071	0.0122	0.0064	0.0065
%sC ₄ (H ₅)	25.4	26.2	27.05	25.46	25.48
$q(\text{C}_4)$	-0.679	-0.689	-0.699	-0.679	-0.680
$q(\text{H}_5)$	0.222	0.245	0.262	0.224	0.222
$r(\text{C}_1 = \text{O}_2)$	1.206	1.212	1.214	1.212	1.218
$\nu(\text{C}_1 = \text{O}_2)$	1808	1789	1783	1788	1764
LPO ₂ → $\sigma^*(\text{C}_1\text{H}_3)$	23.64	22.43	22.22	20.71	18.84
LPO ₁₂ → $\sigma^*(\text{C}_1\text{H}_3)$	—	—	—	—	2.70
LPO ₂ → $\sigma^*(\text{O}_9\text{H}_8)$	—	7.11	9.93	7.35	9.34
LPO ₉ (O ₁₂) → $\sigma^*(\text{C}_4\text{H}_5)$	—	0.46	2.95	—	—
	Isolated H ₂ O	A(1-1)	A(1-2)	B(1-1)	B(1-2)
$r(\text{OH})$	0.9620	0.9711	0.9755 ^a 0.9760 ^b	0.9711	0.9777 ^a 0.9764 ^b
$\nu(\text{H}_2\text{O})$	3926,3820	3894,3681	3889,3629 ^c 3890,3579 ^d	3894,3680	3888,3579 ^c 3890,3603 ^d
$\Sigma q(\text{H}_2\text{O})$	—	-0.017	+0.009 ^e -0.017 ^f	-0.019	-0.004 ^e -0.017 ^f

^aO₉H₈ bond. ^bO₁₂H₁₁ bond. $r(\text{OH} \cdots)$ in the water dimer is 0.9700 Å. ^c $\nu(\text{H}_8\text{O}_9\text{H}_{10})$ ^d $\nu(\text{H}_{11}\text{O}_{12}\text{H}_{13})$, ^e Σq on (H₈O₉H₁₀) ^f Σq on (H₁₁O₁₂H₁₃).

to 0.81 kcal mol⁻¹ in the isolated molecule, 0.71 kcal mol⁻¹ in the A(1-2) complex, and 0.86 kcal mol⁻¹ in the B(1-2) complex. In contrast with the A(1-1) complexes, there is a significant elongation of the C₄H₅ bond in the A(1-2) complexes equal to 0.0012 Å in CH₃CHO, 0.0022 Å in CH₂FCHO and 0.0024 Å in CH₃CFO. The corresponding red shifts of the $\nu(\text{C}_4\text{H}_5)$ vibration are 11, 20 (average value of the ν^{as} and ν^{s} vibrations), and 22 cm⁻¹. It may be interesting to note that the C₄H₅ bond contracts by 0.006 Å when we consider the A(1-1) complex with the C₄H₅ ··· O bond at the trimer geometry and this is mainly due to the increase in % s-character of C₄(H₅) by almost 1.3%. In fact, at the optimized geometry considered here, the cooperativity markedly enhances the LPO₁₂ → $\sigma^*(\text{C}_4\text{H}_5)$ charge transfer, resulting in an elongation of the C₄H₅ bond. Indeed, in CH₃CHO, this charge transfer is equal to 0.46 kcal mol⁻¹ in the A(1-1) complex and 2.95 kcal mol⁻¹ in the A(1-2) complex. This increase is larger in the CH₂FCHO system, being 0.10 kcal mol⁻¹ in the A(1-1) complex and 4.56 kcal mol⁻¹ in the A(1-2) complex. In agreement with this charge transfer, the $\sigma^*(\text{C}_4\text{H}_5)$ occupation increases by amounts ranging from 0.0025e (CH₂FCHO), and 0.0070e (CH₃CFO) with respect to the A(1-1) complexes.

In these cases also, the hybridization of the C₄(H₅) atom slightly increases by ca 1.5% when the C₄H₅ bond is involved

in the A(1-2) interaction, and this increase does not influence the C₄H₅ distances to a great extent.

The C₄H₅ distances are linearly correlated to the $\sigma^*(\text{C}_4\text{H}_5)$ occupation as follows:

$$r(\text{C}_4\text{H}_5)(\text{\AA}) = 0.371\sigma^*(\text{C}_4\text{H}_5)(\text{e}) + 1.0886. \quad (r = 0.973). \quad (3)$$

It should be noticed that in all the systems the C₄H₅ distances where the C₄(H₅) atom has an sp³ hybridization are smaller than the C₁H₃ distances when the C₁(H₃) atom has hybridization between sp^{2.1} and sp^{2.3}. This in contrast with the usual trend for the CH distances: C(sp³)-H > C(sp²)-H. Let us notice that the intercept of (2) (1.0801) is smaller than the intercept of (3) (1.0886). *This possibly reflects the larger CH distances in C(sp³)-H than in C(sp²)-H bonds when the $\sigma^*(\text{CH})$ occupation tends to zero.*

We may also notice that the increase of linearity of the intermolecular O₉H₈ ··· O₂ and C₄H₅ ··· O₁₂ bonds may also contribute to the stability of the trimers.

We will now briefly discuss the changes induced in the water molecules. It is known that the OH bond of the water dimer (O₉H₈ bond in the present systems) is a better proton donor and the O atom (O₁₂ atom in the present systems) is a better proton acceptor than in the water monomer [9–13].

TABLE 2: Properties of the isolated CH₂FCHO and H₂O molecules and the A and B complexes between CH₂FCHO and one and two water molecules (distances in Å, σ^* occupation in e, hyperconjugation energies in kcal mol⁻¹, and frequencies in cm⁻¹).

	Isolated CH ₂ FCHO	A(1-1)	A(1-2)	B(1-1)	B(1-2)
$r(\text{C}_1\text{H}_3)$	1.1096	1.1077	1.1077	1.1065	1.1053
$\nu(\text{C}_1\text{H}_3)$	2914	2938	2938	2958	2975
$\sigma^*(\text{C}_1\text{H}_3)$	0.068	0.063	0.062	0.060	0.056
%sC ₁ (H ₃)	32.1	31.8	31.7	32.5	33.7
$q(\text{C}_1)$	0.408	0.427	0.440	0.421	0.417
$q(\text{H}_3)$	0.117	0.125	0.124	0.141	0.177
$r(\text{C}_4\text{H}_5)$	1.0940	1.0933	1.0962	1.0942	1.0945
$\nu(\text{C}_4\text{H}_5\text{H}_6)$	3096,3045	3106,3058	3077,3024	3094,3044	3090,3041
$\sigma^*(\text{C}_4\text{H}_5)$	0.0199	0.0196	0.0250	0.0200	0.0200
%sC ₄ (H ₅)	25.74	25.97	27.46	25.70	25.61
$q(\text{C}_4)$	-0.011	-0.021	-0.038	-0.011	-0.011
$q(\text{H}_5)$	0.190	0.207	0.246	0.193	0.191
$r(\text{C}_1 = \text{O}_2)$	1.203	1.208	1.210	1.208	1.213
$\nu(\text{C}_1 = \text{O}_2)$	1816	1798	1793	1797	1773
LPO ₂ → $\sigma^*(\text{C}_1\text{H}_3)$	22.94	21.42	21.33	20.83	18.15
LPO ₉ → $\sigma^*(\text{C}_1\text{H}_3)$	—	—	—	—	3.4
LPO ₂ → $\sigma^*(\text{H}_8\text{O}_9)$	—	5.53	6.94	5.51	9.11
LPO ₉ (O ₁₂) → $\sigma^*(\text{C}_4\text{H}_5)$	—	0.10	4.56	—	—
	Isolated H ₂ O	A(1-1)	A(1-2)	B(1-1)	B(1-2)
$r(\text{OH})$	0.9620	0.9696	0.9724 ^a 0.9756 ^b	0.9689	0.9753 ^a 0.9746 ^b
$\nu(\text{H}_2\text{O})$	3926,3820	3896,3725	3893,3676 ^c 3892,3579 ^d	3898,3720	3889,3594 ^c 3892,3631 ^d
$\Sigma q(\text{H}_2\text{O})$	—	-0.013	+0.006 ^e -0.012 ^f	-0.019	0.000 ^e -0.014 ^f

^aO₉H₈ bond. ^bO₁₂H₁₁ bond. ^c $\nu(\text{H}_8\text{O}_9\text{H}_{10})$. ^d $\nu(\text{H}_{11}\text{O}_{12}\text{H}_{13})$. ^e Σq on (H₈O₉H₁₀) ^f Σq on (H₁₁O₁₂H₁₃).

TABLE 3: Properties of isolated CH₃CFO and the 1-1 and 1-2 complexes with H₂O. Distances in Å, σ^* occupation in e, hyperconjugation energies in kcal mol⁻¹, and frequencies in cm⁻¹.

	Isolated CH ₃ CFO	CH ₃ CFO·1H ₂ O	CH ₃ CFO·2H ₂ O
$r(\text{C}_4\text{H}_5)$	1.0877	1.0881	1.0900
$\nu(\text{C}_4\text{H}_5)$	3162	3160	3139
$\sigma^*(\text{C}_4\text{H}_5)$	0.0049	0.0064	0.0122
%sC ₄ (H ₅)	25.4	26.3	27.1
$q(\text{C}_4)$	-0.697	-0.707	-0.716
$q(\text{H}_5)$	0.231	0.257	0.273
$r(\text{C}_1 = \text{O}_2)$	1.182	1.188	1.189
$\nu(\text{C}_1 = \text{O}_2)$	1912	1884	1875
LPO ₁₂ → $\sigma^*(\text{C}_4\text{H}_5)$	—	0.78	3.56
LPO ₂ → $\sigma^*(\text{O}_9\text{H}_8)$	—	4.10	6.67
	Isolated H ₂ O	CH ₃ CFO·1H ₂ O	CH ₃ CFO·2H ₂ O
$r(\text{OH})$	0.9620	0.9677	0.9710 ^a 0.9756 ^b
$\nu(\text{H}_2\text{O})$	3926,3820	3901,3748	3891,3704 ^c 3890,3600 ^d
$\Sigma q(\text{H}_2\text{O})$	—	-0.008	+0.009 ^e -0.014 ^f

^aO₉H₈ bond. ^bO₁₂H₁₁ bond. ^c $\nu(\text{H}_8\text{O}_9\text{H}_{10})$. ^d $\nu(\text{H}_{11}\text{O}_{12}\text{H}_{13})$. ^e Σq on (H₈O₉H₁₀). ^f Σq on (H₁₁O₁₂H₁₃).

For NBO charges on H and O atoms in the monomer, dimer, and complexes, see S.I.).

As previously mentioned, the intermolecular $O_9 \cdots H_{11}$ distances do not markedly differ in the 1-2 complexes. From this, it can be anticipated that the properties of the water dimer considered as subsystem will not vary on a spectacular way. For all the complexes, the results indicate that the bonds between the two water molecules is stronger than in the water dimer. Further, as indicated in Tables 1, 2, and 3, the $C=O \cdots HO$ bond in the 1-2 complexes is stronger than in the 1-1 complexes. This is shown by the larger elongation of the O_9H_8 bond, the larger decrease of the corresponding vibrational frequencies, and the larger $LPO_2 \rightarrow \sigma^*(O_9H_8)$ hyperconjugation.

The elongations of the OH bond are linearly related to frequency shifts of the $\nu^s(OH)$ vibration of water as follows:

$$\Delta r(OH)(\text{\AA}) = 5.10^{-5} \Delta \nu^s(OH)(\text{cm}^{-1}) + 0.0029 \quad (r = 0.978). \quad (4)$$

This correlation includes all the 1-1 and 1-2 complexes.

Other water properties such as the $\sigma^*(OH)$ occupation are summarized in S.I. These results indicate a large positive NBO charge of the bonding protons H_8 and H_{11} , a larger negative charge on the O_9 or O_{12} atoms, and a larger $\sigma^*(O_9H_8)$ or $\sigma^*(O_{11}H_{12})$ occupation than in the 1-1 complexes. It should be also noticed that in the 1-1 complexes, the water molecule acts as an electron acceptor, with the charge transfer from the carbonyl derivative to the water molecule ranging from 0.008 to 0.017e. In the 1-2 complexes, the sum of the charge on the $H_8O_9H_{10}$ molecule remains weak (positive or negative), the charge being transferred to the second water molecule which always bears a negative charge.

3.3. Binding Energies. Table 4 reports the total binding energies in the trimer, $E(ABC)$; the binding energies between the AB, BC, and AC molecules at the trimer geometry along with the cooperative energies, ΔE^{coop} , calculated by (1).

The % cooperativity defined as the ratio $\Delta E^{\text{coop}}/E_{\text{ABC}}$ ranges between 18% and 20% and is almost constant for the five systems considered here. This percentage is slightly larger than in the $H_2C=O \cdot 2H_2O$ system (16%) [27] but smaller than in the $NH_2CHO \cdot 2H_2O$ system (26%) where the $C=O \cdots HO$ and $CH \cdots O$ bonds are formed [20].

The binding energies between the two water molecules are almost the same for all the systems, between -4.50 and $-4.62 \text{ kcal mol}^{-1}$. These results are in line with the small differences in intermolecular distances and the NBO parameters in the two bonded water molecules discussed in the previous section.

The binding energies E_{AB} vary between -4.73 and $-3.60 \text{ kcal mol}^{-1}$. They are ordered according to the proton affinities of the O atom of the carbonyl group which vary from 170.1 to 185.3 kcal mol^{-1} (Table 4)

$$-E_{\text{HB}}(\text{kcal mol}^{-1}) = 0.0786 \text{ PA}(\text{kcal mol}^{-1}) - 9.83 \quad (r = 0.998). \quad (5)$$

TABLE 4: B3LYP/6-311++G(d,p) Total Binding Energies (E_{ABC} , E_{AB} , E_{BC} , and E_{CA} binding energies in the trimer geometry and cooperative energies (ΔE_{coop}) for the CH_3CHO , CH_2FCHO , and CH_3CFO complexes with two water molecules (with BSSE-corrections in kcal mol^{-1})^a.

System	E_{ABC}	E_{AB}^{b}	E_{AC}	E_{BC}	ΔE_{coop}
$\text{CH}_3\text{CHO} \cdot 2\text{H}_2\text{O}$ (A)	-13.04	-4.64 (183.8)	-1.52	-4.56	-2.32
$\text{CH}_3\text{CHO} \cdot 2\text{H}_2\text{O}$ (B)	-13.48	-4.73 (185.3)	-1.66	-4.50	-2.59
$\text{CH}_2\text{FCHO} \cdot 2\text{H}_2\text{O}$ (A)	-13.00	-3.60 (170.1)	-2.31	-4.59	-2.50
$\text{CH}_2\text{FCHO} \cdot 2\text{H}_2\text{O}$ (B)	-12.49	-3.71 (172.4)	-1.72	-4.54	-2.52
$\text{CH}_3\text{CFO} \cdot 2\text{H}_2\text{O}$ (A)	-12.41	-3.60 (171.4)	-1.87	-4.62	-2.32

^aA = carbonyl derivative, B and C = water. ^bThe numbers in parentheses are the Proton Affinities of the O atom of the $C=O$ group (kcal mol^{-1}) taken from [22].

The slope of this correlation is slightly larger than the slope of the correlation calculated for the 1-1 complexes (0.061) [22]. This conclusion must be taken with caution owing to the small range of considered energies. In a broad energy range, the cooperativity effects are usually nonlinear [49].

Let us also notice that the C_4H_5 bonds characterized by deprotonation enthalpies between 357 and 364 kcal mol^{-1} are better proton donors than the C_1H_3 bonds having much larger deprotonation enthalpies, between 382 and 391 kcal mol^{-1} . The binding energies E_{AC} are weak but do not reflect the differences in acidity of the CH bonds. The same remark also holds for the % of cooperativity which is almost constant.

4. Conclusions

The present work deals with a theoretical investigation of the cooperativity in $\text{CH}_3\text{CHO} \cdot 2\text{H}_2\text{O}$, $\text{CH}_2\text{FCHO} \cdot 2\text{H}_2\text{O}$, and $\text{CH}_3\text{CFO} \cdot 2\text{H}_2\text{O}$ systems. The results are compared with the complexes involving one water molecule. The main conclusions of our work are the following ones.

- (1) For the three systems, two stable cyclic structures are predicted. Both structures are stabilized by $C=O \cdots HO$ interaction. In the A structures, the system is stabilized by a $CH \cdots O$ interaction involving the CH_3 (or CH_2F) group. In the B structures, the CH bond of the HC=O group participates to the $CH \cdots O$ interaction. The optimized structures indicate shorter intermolecular distances than in the 1-1 complexes or than in the water dimer.
- (2) Formation of the A(1-2) complexes results in an elongation of the CH bond of the CH_3 or CH_2F group involved in the $CH \cdots O$ interaction, a red shift of the $\nu(\text{CH})$ vibration, and an increase in occupation of the $\sigma^*(\text{CH})$ orbitals. This elongation is negligible in the A(1-1) complexes. In contrast,

formation of the B(1-2) complexes results in a contraction of the aldehydic CH bond and a marked blue shift of the $\nu(\text{CH})$ vibration, which are both larger than in the B(1-1) complexes. This effect is explained by a large decrease of the intramolecular LPO $\rightarrow \sigma^*(\text{CH})$ hyperconjugation energy and illustrates the predominance of the lone pair effect in determining the CH distances.

- (3) The elongation of the OH bonds in the water molecules, the red shifts of the $\nu(\text{OH})$ vibrations are larger than in the water dimer. The same remark also holds for the variation of the NBO charges on the H and O atoms.
- (4) Quantitative correlations between the CH distances and the $\sigma^*(\text{CH})$ occupations or between the frequency shifts of the $\nu(\text{OH})$ stretching vibrations and the elongations of the OH bond of water are presented.
- (5) The total binding energies in the ternary systems range between -12.41 and -13.48 kcal mol $^{-1}$. The two-body interaction energies are calculated at the trimer geometries. At this geometry, the interaction energies between the carbonyl derivative and the considered water molecules slightly increase with the basicity of the C=O group. The cooperative energies are comprised between -2.32 and -2.59 kcal mol $^{-1}$.

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