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Ab Initio Study of the Structures and $\pi^* \leftarrow n$ Electronic Transition in Formic Acid−(Water)$_n$ (n = 3, 4, and 5) Hydrogen Bonded Complexes

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Hydrogen-bonded complexes of formic acid-$(H_2O)_n$ (n = 3, 4, and 5) have been studied using multiconfigurational SCF and second-order perturbation theory, (CASSCF/CASPT2). Equilibrium geometries in the ground electronic state S_0, and vertical $S_1 \leftarrow S_0$ transition energies have been calculated for the 1:3, 1:4, and 1:5 complexes. Similar results for energetics and geometry of the ground state were obtained with Becke3LYP calculations. The vertical transitions are blue-shifted with respect to the corresponding monomer transition, and their dependence on the number of water molecules is not monotonic.

1. Introduction

Hydrogen bonding is of paramount importance in molecular sciences for practical and theoretical reasons. It largely determines the physical properties of many common condensed phase systems including water. It represents the strongest force governing the influence of solvents on molecular structure and reactivity, and a quantitative account for hydrogen-bonding interactions is necessary for the proper understanding of chemical activity taking place in aqueous solution. Hydrogen bonding has been of particular interest in recent years due to the central role it plays with regard to molecular recognition in both biological and artificial systems.[1,2]

Water is the prototype for the study of the hydrogen bond and for this reason it has received a great deal of attention from both theoretical[3−6] and experimental points of view.[7−10] Also, water can form small clusters[11] that are of great interest due to its importance as an omnipresent solvent in chemical and life processes. The structures of biomolecules are influenced by the inner hydration layers, leading in turn to changes in the biological activity.

To examine the effect of the number of water molecules on the properties of this kind of complexes, many studies were made with different molecules such as formanilide,[12] indole,[13] 7-hydroxyquinoline,[14] and benzene.[15,16] Formic acid, HCOOH, is the simplest carboxylic acid and is interesting in many aspects. In the gas phase it has been observed the formation of dimers of HCOOH with two hydrogen bonds in a planar eight-membered ring. The dimer of HCOOH has been studied by experimental[17−19] and theoretical methods.[20−24] Clusters of water and formic acid have been studied by electron impact[25] and by microwave spectroscopy.[26] The double proton transfer and the structure of transition state have been studied in 1:1 complex and the structures of ground and transition states have been also obtained for 1:1 and 1:2 complexes of formic acid−water by ab initio calculations RHF/6-31G** and MP2(full)/6-31G** levels of theory[27] and HF/6-31+G* level.[28] Recently, the structures of the most stable 1:1 and 1:2 conformers of formic acid−water have been calculated.[29−31]

The molecules with carbonyl groups show a blue shift in the $\pi^* \leftarrow n$ transition in a polar solvent, as it has been observed in the case of acetone−water,[32] formaldehyde-(water)$_n$,[33,34] and HCOOH−(water)$_n$.[31] The origin of the blue shifts could be attributed to the considerable weakening of the hydrogen bond in the excited state and to the loss of electrostatic energy, mainly due to the flux of charge density from the O to C in the C═O group in the S_1 electronic state.[35]

In this work we present a study of the structures and $\pi^* \leftarrow n$ electronic transitions in formic acid−$(H_2O)_n$ (n = 3, 4, and 5) hydrogen-bonded complexes using the complete active space SCF method, CASSCF,[36] and multiconfigurational second-order perturbation theory, CASPT2.[37] This method has been applied to a variety of chemical problems in last years and has shown to give accurate results for molecular structures, binding energies and other properties not only for molecules with normal chemical bonds, but also for molecules in excited states and for weakly bonded systems. We have also performed Becke3LYP calculations for the ground state with very similar results.

The paper is organized as follows. Section 2 presents the methodology, section 3 is devoted to the discussion of the results, and section 4 presents the conclusions.

2. Methodology

The calculations were made following the same procedure than in the previous paper on this subject.[31] To find the different conformers of HCOOH−$(H_2O)_n$, (n = 3, 4, and 5), the ground potential energy surface landscapes of the complexes has been explored in a first approximation by performing HF/6-31G** calculations with *Gaussian 98*.[38] With these initial inputs, the geometries of different conformers were optimized at a CASSCF level of theory. The CASSCF formulation stresses the effects of nondynamic correlation.[39−41] The geometry of different

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TABLE 1: Geometrical Parameters of Formic Acid Isolated and Complexes in Their Electronic Ground State, S_0 at CASSCF Level[a]

	$C_{1:3}$	$C_{1:4}$	$C_{1:5}$	HCOOH
$H_1{-}C_2$	1.087 (1.101)	1.085 (1.099)	1.097 (1.101)	1.083 (1.098)
$C_2{-}O_3$	1.297 (1.309)	1.307 (1.324)	1.319 (1.311)	1.193 (1.342)
$C_2{-}O_5$	1.188 (1.222)	1.191 (1.220)	1.227 (1.221)	1.332 (1.205)
$O_3{-}H_4$	0.965 (1.021)	0.961 (1.004)	0.961 (1.026)	0.955 (1.199)
$\angle H_1{-}C_2{-}O_3$	111.1 (110.9)	111.2 (110.9)	110.6 (110.7)	110.6 (109.2)
$\angle H_1{-}C_2{-}O_5$	122.4 (121.2)	123.1 (122.8)	121.8 (121.3)	124.6 (125.4)
$\angle O_5{-}C_2{-}O_3$	126.5 (127.8)	125.7 (126.3)	127.6 (128.0)	124.8 (124.9)
$\angle C_2{-}O_3{-}H_4$	112.7 (113.8)	110.1 (108.0)	111.6 (113.3)	109.8 (106.7)
$O_5{\cdots}H_6$	1.949 (1.763)	2.171 (1.941)	1.966 (1.817)	
$O_7{\cdots}H_9$	1.870 (1.709)		1.937 (1.784)	
$O_{10}{\cdots}H_{12}$	1.857 (1.665)		1.799 (1.626)	
$O_{13}{\cdots}H_4$	1.764 (1.567)		1.743 (1.574)	
$H_8{\cdots}O_9$		1.855 (1.679)		
$H_{10}{\cdots}O_{12}$		1.883 (1.712)		
$H_{13}{\cdots}O_{15}$		1.899 (1.740)		
$H_{16}{\cdots}O_7$		1.956 (1.761)		
$O_7{\cdots}H_4$		1.888 (1.725)		
$H_{11}{\cdots}O_{15}$			1.947 (1.795)	
$H_{16}{\cdots}O_{18}$			1.960 (1.828)	

[a] The distances are in angstroms and angles in degrees. The values obtained by B3LYP/6-31G** are in parentheses.

conformers has been optimized without symmetry constraints to yield energy minima with C_1 symmetry using an atomic natural orbitals (ANO) basis set[42−45] provided by the *MOLCAS 4.0* program.[46] For the calculations, the number of active orbitals was 2 (the last occupied and the first unoccupied) and the number of active electrons was 2 (valence electrons). The rest of orbitals is taken as inactive.

It is well-known that the reliably accurate desription of weak interactions generally requires a treatment of electronic correlation.[30] Density functional methods have proved quite useful in this regard for hydrogen bonded complexes.[47] The B3LYP functional in particular was highly effective in many systems with hydrogen bondings.[48,49] To test the CASSCF optimizations, the different conformers have also been optimized at B3LYP/6-31G** level of theory using *GAUSSIAN-98*.[38] We have found the same minima as those obtained at CASSCF level with slight differences in geometries and energies. The calculated bond lengths and angles are given in Table 1 for the HCOOH−$(H_2O)_n$, ($n = 3$, 4 and 5) complexes and the energies of the complexes are shown in Table 2. Using the CASSCF wave function as a reference function, the CASPT2 method was used to compute the first-order wave functions and the second-order energies in the full CI space without any other approximation. The basis-set, symmetry, and orbitals were the same as those in CASSCF calculations.[50,51]

The binding energy for the different conformers were computed as

$$\mathrm{BE} = E(\text{complex}) - E(\text{HCOOH}) - nE(\text{H}_2\text{O}) \qquad (1)$$

where E(HCOOH) and $E(H_2O)$ have been calculated separately at the optimized ground-state geometry at the same level of theory. E(complex), E(HCOOH), and $E(H_2O)$ in eq 1 include the corresponding zero point energy (ZPE). ZPE was estimated by its simplest approximation:

$$\mathrm{ZPE} = (^1/_2)\sum_i h\nu_i \qquad (2)$$

where ν_i is the frequency for mode i obtained at the optimized geometry and then we used a scale factor of 0.9 for the corrections on energy.[52] The binding energies defined in this way are affected by the basis set superposition error (BSSE), which has been estimated using the counterpoise procedure.[53−56] The counterpoise correction is an approximate but satisfactory method for correcting basis set deficiencies in the calculations of the monomers.[57] This method has been discussed in the literature at large and there are arguments in favor and against the counterpoise correction. A discussion of these different approaches is beyond the scope of this article.[55] The values of the minima and binding energies are in Table 2.

For the optimized geometries of the conformers, the first vertical transitions $S_1 \leftarrow S_0$, ΔE_V, were calculated at CASSCF and CASPT2 level of theory. In the calculation of the S_1 energy with S_0 geometry, the number of active orbitals was 5 and the number of active electrons was 6 (valence electrons): two orbitals with 2 electrons, two orbitals with 1 electron and the last one unoccupied. The rest of orbitals were taken as inactive.

The values of ΔE_V are also affected by the BSSE and the corresponding counterpoise correction has to be performed. To calculate this correction it was assumed that the $S_1 \leftarrow S_0$ transition in the complexes is localized on HCOOH. In the ground state, GS, the counterpoise correction is given by

$$CP_{\mathrm{GS}} = E(\text{complex}) - E(\text{HCOOH})_{\mathrm{w}} - E(w)_{\mathrm{HCOOH}} \qquad (3)$$

where $E(\text{HCOOH})_{\mathrm{w}}$ is the energy of the formic acid including the orbitals of water molecules (ghost orbitals)[46] and $E(w)_{\mathrm{HCOOH}}$

TABLE 2: Total Energies (E, in hartree), Zero Point Energies (ZPE, in hartree), Total Energies Corrected by ZPE (E_{ZPE}, in hartree), Binding Energies (BE, in kJ/mol), Binding Energies Corrected by Counterpoise Method (BE_{CP}, in kJ/mol), Counterpoise Correction (CP, in kJ/mol), Rotational Constants and Electric Dipole Moment, $|\mu|$, for Complexes HCOOH−$(H_2O)_n$, $n = 3$, 4, and 5[a]

		$C_{1:3}$	$C^2_{1:3}$[a]	$C_{1:4}$	$C_{1:5}$
HF/6-31G**	E	−416.87165		−493.05908	−568.87463
MP2/6-31G**	E	−418.10875		−494.48777	−570.31666
B3LYP/6-31G**	E	−419.08894	−419.08725 (4.22)[b]	−495.48083	−571.89646
CASSCF	E	−417.05630	−417.05473 (4.12)	−493.26831	−569.11044
CASPT2	E	−418.23099	−418.22942 (4.13)	−494.66982	−570.77327
	ZPE	0.117 69		0.082 45	0.160 10
	E_{ZPE}	−418.12507		−494.59561	−570.62918
	BE	−222.6		−251.0	−284.2
	BE_{CP}	−176.4		−240.6	−273.5
	CP	46.2		10.4	10.7
	A/GHz	2.588		2.698	1.730
	B/GHz	1.474		0.594	0.369
	C/GHz	0.951		0.531	0.349
	$\lvert\mu\rvert$/D	0.890		0.968	4.308

[a] $C^2_{1:3}$ is the proposed structure in ref 58. [b] The values in parentheses correspond to the difference on energy between $C^2_{1:3}$ and $C_{1:3}$ in kJ per mole.

TABLE 3: Thermodynamical Properties for the Process nH$_2$O + HCOOH → HCOOH−(H$_2$O)$_n$, for n = 1−5 at MP2/6-31G Level**[a]

complex	ΔH/kJ mol^{-1}	ΔG/kJ mol^{-1}	ΔS/kJ mol^{-1} K^{-1}
1:1	−81.6	−36.1	−0.1525
1:2	−176.6	−86.6	−0.3019
1:3	−261.4	−153.4	−0.3623
1:4	−385.3	−215.5	−0.5697
1:5	−490.5	−318.3	−0.5776

[a] The temperature is 298.15 K.

is the energy of water molecules including the orbitals of HCOOH. In the excited state,

$$CP^* = E(\text{complex}^*) - E(\text{HCOOH}^*)w - E(w)_{\text{HCOOH}} \quad (4)$$

The counterpoise correction for the energy of the vertical transition has then been calculated as

$$\begin{aligned} CP_{\text{V}} &= CP^* - CP_{\text{GS}} \\ &= E(\text{complex}^*) - E(\text{complex}) \\ &\quad - [E(\text{HCOOH}^*)_{\text{w}} - E(\text{HCOOH})_{\text{w}}] \end{aligned} \quad (5)$$

The values of vertical transitions and their corrections are shown in Table 3. In all the cases, the values of ΔE_{V} are blue shifted with respect to the isolated HCOOH and the counterpoise correction is about 10% of the blue shifts.

3. Results and Discussion

3.1. Ground State's Conformers. We have explored the geometry of the conformers for n = 3, 4, and 5 molecules of water, and we have found one conformer for each case (Table 1). We have tried several initial configurations for the calculations of geometry optimization. In these trial geometries we did not considered any structures involving an interaction between the H atom in the H−C bond of formic acid with water on the basis of previous finding that its contribution to the binding energy in the 1:1 and 1:2 complexes are negligible.[31] As an example of this situation we optimized a geometry in the 1:3 complex involving the following H-bonds: $O_{13}\cdots H_4$, $O_5\cdots H_6$, and $O_{10}\cdots H_1$, which corresponded to a minimum according to an AM1 calculation.[58] This structure, $C^2_{1:3}$, was used as an input for CASSCF and B3LYP/6-31G** optimization. Comparing the values of the energy for $C_{1:3}$ (Figure 1a) and $C^2_{1:3}$, we have found that $C^2_{1:3}$ is 4.13 kJ mol^{-1} higher than $C_{1:3}$, and a similar result (4.43 kJ mol^{-1}) is obtained at B3LYP/6-31G** level. The mentioned H-bonds are longer than 2 Å. As a consequence, we have not considered this kind of structures and the same idea was used for the 1:4 and 1:5 complexes. Also, we can note that the CASSCF and B3LYP/6-31G** results are very similar. In the case of the 1:3 complex (Figure 1a), the three water molecules form a bridge between the C=O and H−O groups in formic acid, giving a 10-membered ring structure with four H-bonds: $O_5\cdots H_6$ = 1.949 Å, $O_7\cdots H_9$ = 1.870 Å, $O_{10}\cdots H_{12}$ = 1.857 Å, and $O_{13}\cdots H_4$ = 1.764 Å. Comparing with the geometry of free HCOOH, it can be seen that $C_2{=}O_5$ is shorter, $C_2{-}O_3$ is larger, and the angle $O_5{-}C_2{-}O_3$ is 2° wider in the complex while the other bonds remain essentially unchanged. The binding energy of this complex is 176.4 kJ mol^{-1} with BSSE correction.

In the case of 1:4 conformer (Figure 2a), the water molecules form a ring that interacts with formic acid through two H-bonds: $O_5\cdots H_6$ = 2.171 Å, $O_7\cdots H_4$ = 1.888 Å. The other four H-bonds are between the water molecules: $H_8\cdots O_9$ = 1.855 Å, $H_{10}\cdots O_{12}$ = 1.883 Å, $H_{13}\cdots O_{17}$ = 1.899 Å, and $H_{16}\cdots O_7$ = 1.888 Å. The $C_2{-}O_3$ is larger and $C_2{=}O_5$ is shorter than in the case of free formic acid. The angle $O_5{-}C_2{-}O_3$ is 1° wider. The dihedral angle $\angle C_2{-}O_3{-}O_7{-}O_{15}$ is 121.4°. This structure is similar to that found by Fedorov et al. in formanilide-(water)$_4$ complex.[12] The binding energy is 240.6 kJ mol^{-1} with BSSE correction.

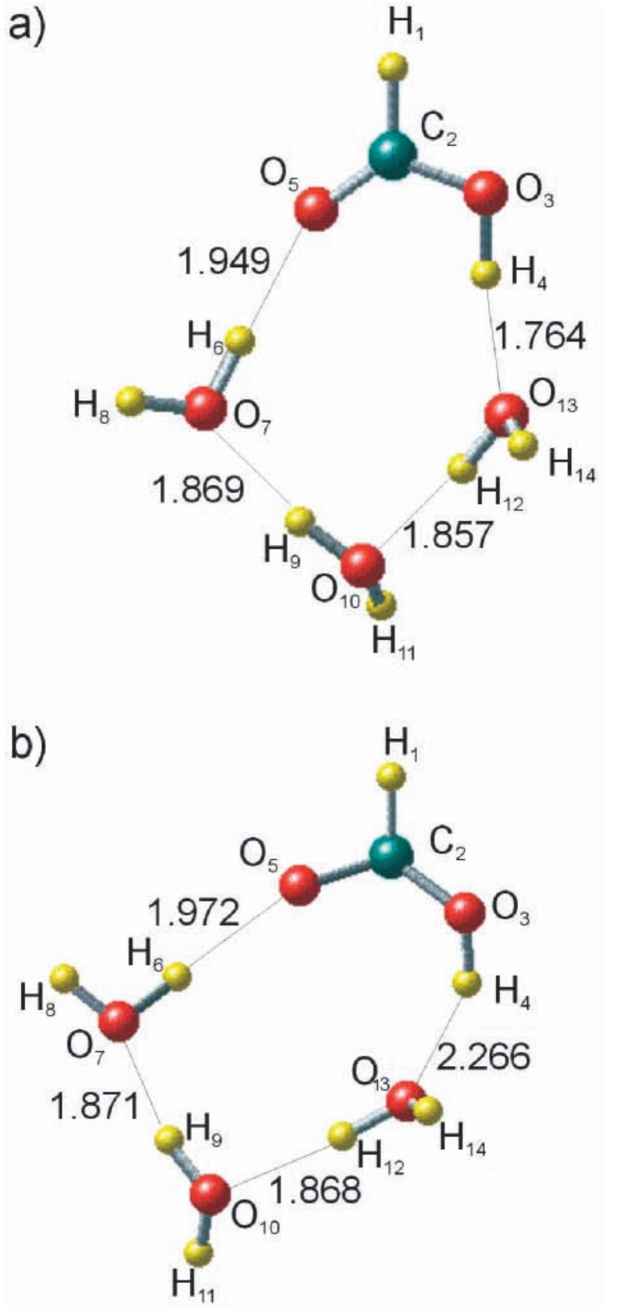

Figure 1. Geometries of the HCOOH−(H$_2$O)$_3$ on (a) S$_0$ and (b) S$_1$ electronic states, respectively. The distances of H-bonds are showed in angstroms.

In the case of the 1:5 (Figure 3) complex, the water molecules form two groups: the first one consists of three water molecules bonded to formic acid in a similar fashion to that of the 1:3 complex. And the second group is formed by two water molecules that interacts with one water of the first ring. The inner H-bonds are $O_5\cdots H_6$ = 1.874 Å, $O_7\cdots H_9$ = 1.834 Å, $O_{10}\cdots H_{12}$ = 1.681 Å, and $O_{13}\cdots H_4$ = 1.622 Å. The external H-bonds are $H_{11}\cdots O_{15}$ = 1.843 Å and $H_{16}\cdots O_{18}$ = 1.877 Å. The geometry of formic acid in the complex has a similar behavior

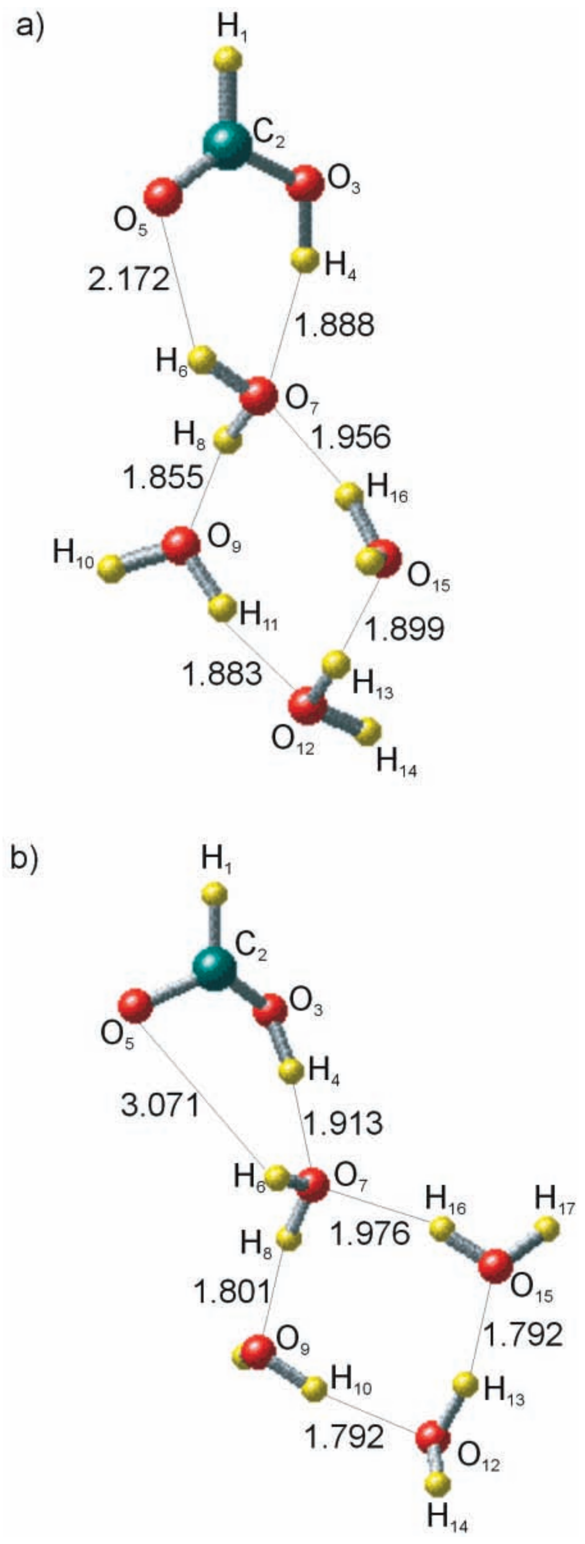

Figure 2. Geometries of the $HCOOH-(H_2O)_4$ on (a) S_0 and (b) S_1 electronic states, respectively. The distances of H-bonds are showed in angstroms.

than in the other complexes. The dihedral angle $\angle O_{15}-O_{10}-O_{13}-O_7$ is 105.6°. The binding energy with BSSE correction is 273.5 kJ mol^{-1}.

Also, thermodynamical properties for the process $n H_2O + HCOOH \rightarrow HCOOH-(H_2O)_n$, were calculated at MP2/6-31G** at 298.15 K (Table 3). The values of 1:1 and 1:2 are based on a previous calculation.[31] The values show a monotonic increase with the number of molecules of water.

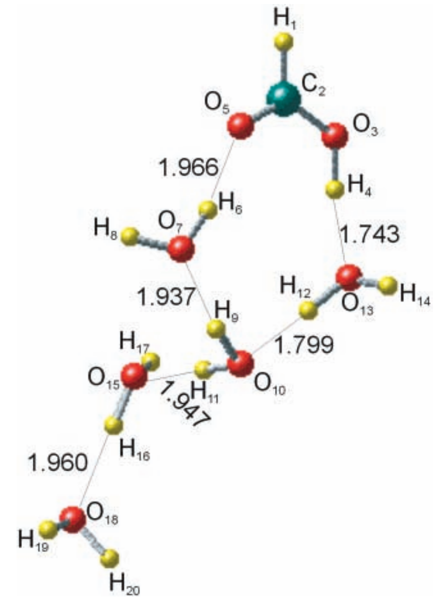

Figure 3. Geometry of the $HCOOH-(H_2O)_5$ on S_0 electronic state. The distances of H-bonds are showed in angstroms.

3.2. Vertical Transitions $\pi^* \leftarrow n$ and Origin Bands. With the optimized geometries of HCOOH and $HCOOH-(H_2O)_n$ ($n = 3$, 4, and 5) in their electronic ground state S_0, we have calculated the CASPT2 excitation energies ΔE_V for the vertical transitions $\pi^* \leftarrow n$ (Table 3). Since we are motivated by the experiments performed at very low temperature in supersonic expansions,[10] we have taken $T = 0$ K.

For free HCOOH, we have obtained $\Delta E_V = 5.82$ eV at CASPT2 level which is in agreement with the values obtained by Iwata et al. who used the electron−hole potential.[21] The values of ΔE_V are blue-shifted respect to free HCOOH. The blue shift obtained indicate the destabilization of the excited state S_1 with respect to the ground state due to the loss of electrostatic interaction energy between the atoms weakening the H-bonds. This behavior was also observed in aldehydes and ketones and is caused by a loss of electrostatic energy in the excited state with respect to the ground state.[34] The electrostatic energy was calculated as

$$\Delta E_{\mathrm{coulomb}} = \sum_{i}^{\mathrm{water}} \sum_{j}^{\mathrm{HCOOH}} q_i q_j / r_{ij} \tag{6}$$

where q_i are the net atomic charges in H_2O, q_j are the net charges in HCOOH, and r_{ij} is the distance between the atoms.

To provide a simple interpretation of the results, the charge distribution per atom and basis function have been obtained by Mulliken[46] and natural population analysis.[3] In both cases, the Coulombic energy decreases for all the complexes in the excited state as it can be seen in Figure 4. Upon analyzing the values of ΔE_V on the number of molecules of water, it can be observed that for $n \geq 3$ molecules of water, the values of ΔE_V remain constant similarly to the case of the complexes of benzene−(water)$_n$[16]. This indicates that there is a limit to the number of molecules of water that can interact directly with the chromophore group, C=O. These water molecules form a first hydration layer while the rest of molecules above that maximum number forms a net that interacts directly with it but not with the acid.

We also have calculated the origin band ΔE_o for 1:3 and 1:4 complexes and free HCOOH. Because of problems of convergence in the calculation for 1:5 complex, the value of ΔE_o was

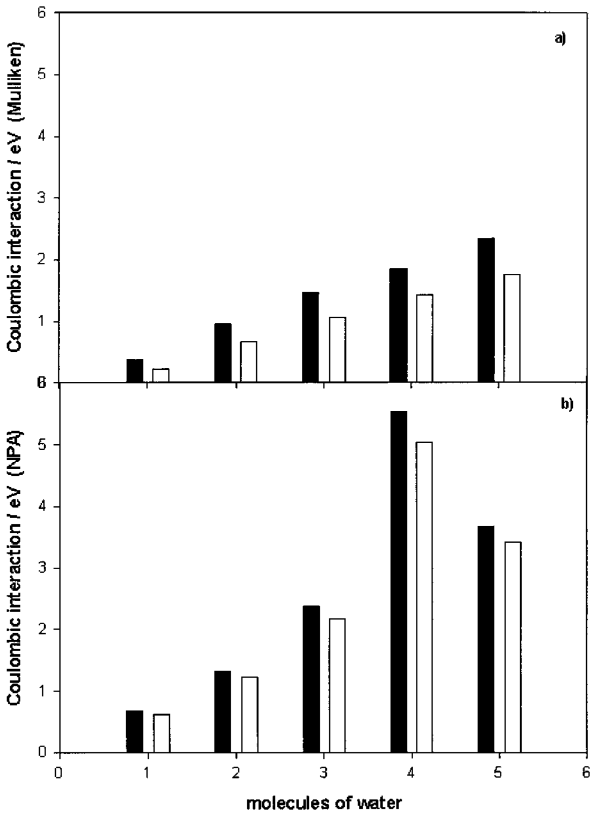

Figure 4. Comparison between electrostatic energy of S_0 (○), and S_1 (●), electronic states of the complexes HCOOH−$(H_2O)_n$, $n = 1-5$. (a) Mulliken population analysis. (b) Natural population analysis. The values for $n = 1$ and 2 are taken from ref 30.

TABLE 4: Vertical Transitions without, ΔE_V, and with Counterpoise Correction, ΔE_V^{CP}, and Origin Bands, ΔE_o, of Isolated HCOOH and HCOOH−$(H_2O)_n$, $n = 1-5$, Complexes, at CASPT2 Level

complex	ΔE_V/eV	ΔE_V^{CP}/eV	ΔE_o/eV	ref
HCOOH (exptl)	**5.83**		**4.64**	59
			4.78	60
HCOOH (calcd)	5.82		4.61	31
1:1	6.26	6.31	4.81	31
1:2	6.16	6.19		31
1:3	6.14	6.17	4.84	this work
1:4	6.36	6.40	5.00	this work
1:5	6.26	6.29		this work

not obtained. The results are presented in Table 4. For free HCOOH, the value of ΔE_o is 4.61 eV, which is in agreement with the experimental value of Ioannoni[59] (4.64 eV) and Ng et al.[60] (4.78 eV). The values of ΔE_o for the complexes 1:3 and 1:4 are blue shifted with respect to free HCOOH. This effect was also observed for 1:1 and 1:2 complexes.[31]

The blue shift seems to be a consequence of the destabilization of the excited state with respect to the ground state because there is a change of hybridization on C (sp^3 in S_1 state) of formic acid and a weakening of the H-bonds. In Figures 1b and 2b, the changes in the geometry of HCOOH in the 1:3 and 1:4 can be seen. The dihedral angle $O_5-C_2-O_3-H_4$ changes from almost 0° in S_0 state to 57° and 68° in 1:3 and 1:4 complexes, respectively. The H-bonds distances between water and formic acid are bigger than those in the S_0 state.

By examining the change of the net charge of the atoms, particularly in the carbonyl group, we observed that there is a transfer of negative charge from O to C when the system is on S_1 surface.

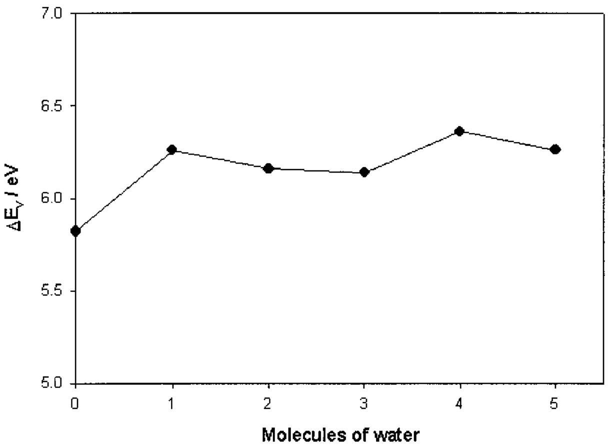

Figure 5. Values of the energy of the electronic vertical transitions in free formic acid and the complexes HCOOH−$(H_2O)_n$, $n = 1-5$. The values for $n = 1$ and 2 are taken from ref 31.

4. Conclusions

In this work we have calculated vertical $\pi^* \leftarrow n$ transitions of different conformers of HCOOH−$(H_2O)_n$, ($n = 3$, 4, and 5) complexes. Using CASSCF for the optimization of the geometry, similar results for energetics and geometry were obtained by DFT(B3LYP) calculations. We have to note that the minimum we have found for each complex is not necessary an absolute minimum, in particular for larger clusters, and in future work it will be necessary to perform a full search using semiempirical potentials.

The results indicate that there are two groups of water molecules depending on whether they interact directly with the carbonyl group of the formic acid or they are outside this region and start to form a second layer. This fact is observed in 1:3 and 1:5 complexes. The 1:4 complex is a special case where the molecules of water form a square that interacts with HCOOH through two H-bonds in a similar fashion than formanilide−(water)$_4$.[12]

Regarding the vertical transitions, it was found that they are blue shifted with respect to isolated HCOOH. This is due to the decreasing of the electrostatic energy in the excited state with respect to the ground state. This effect is also observed in the origin bands. In the excited state, the C atom changes its hybridization to sp^3, leading to an increase in the distance C_2-O_5 and a weakness of the H-bond interaction with the molecules of water. Other effect is that it can be seen that the energy of this transition does not rise with the number of molecules of water (Figure 5), for $n \geq 3$. This effect was also observed in the complexes of formaldehyde−(water)$_n$.[35] The excess of water molecules does not induce an increase in the values of ΔE_V because the rest of molecules of water interact between them and not with the carbonyl group.

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