Ab Initio Investigation of Vibrational Spectra of Water−$(CO_2)_n$ Complexes (n = 1, 2)

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In this paper, we have calculated using the ab initio method the IR vibrational spectra of complexes of CO_2 formed with water (sp^3 O-donating atom). Binding energies and structures of the CO_2−H_2O and water−$(CO_2)_2$ complexes have been determined at the second-order level of the Moller−Plesset perturbation theory (MP2) using Dunning's basis sets. The results are presented and critically discussed in terms of the nature of the water−CO_2 interactions, electron donor acceptor (EDA) and weak O···H−O interactions. For water−$(CO_2)_2$ trimer, it is also shown that the contribution to the interaction energy of the irreducible three-bodies remains relatively negligible. We have analyzed the frequency shifts and the IR and Raman intensity variations under the complex formation. We have particularly emphasized the splitting of the ν_2 bending mode of CO_2 and stretching modes of water, which have been revealed as the most pertinent probes to assess the nature of the forces involved in the different complexes. Finally, because water can play the role of Lewis base and acid as well, we found that weak O···H−O interactions can cooperate with EDA interactions in trimer, leading to very specific spectral signatures that are further discussed.

1. Introduction

Understanding interactions of carbon dioxide with water is of wide interest in many research fields such as physical, biochemical, and atmospheric chemistry. Therefore, this system has been the subject of a large body of experimental and theoretical studies concerning the hydration of CO_2 and the solvation of H_2O.[1−7] In the presence of Lewis bases such as water, alcohols, ketones, amines, and amides, CO_2 acts as a Lewis acid favoring the formation of electron donor−acceptor (EDA) complexes.[8−12] This is due to the electron deficiency of the C atom of CO_2 and bond electron density more polarized toward the O atoms. Investigations on the nature of interactions of CO_2 with organic solutes in gaseous and liquid phases have firmly shown the adequateness of combining infrared (IR) absorption and Raman scattering measurements with ab initio calculations.[8,10−12] Evidence coming from vibrational spectroscopy and theoretical chemistry led to the conclusion that molecules having at least an electron donor center favorably interact with CO_2. These studies have been recently extended to solutes dissolved in supercritical CO_2.[13,14] Using supercritical (SC) fluids as solvents offers the advantage to investigate solvation mechanisms by varying their physical and transport properties with the density. Indeed, above the critical temperature of the solvent, the density of the fluid can be continuously varied from gas-like to liquid-like values without phase transition. Therefore, SC fluids enable us to improve our understanding of EDA interactions in condensed phases by bridging the existing gap of physical observables between vapor and liquid state. Recent IR and Raman spectroscopic studies combined with ab initio computations revealed strong implications of transient EDA complexes in the solvation process in SC CO_2.[10,15−21]

Although water mainly interacts with CO_2 as a Lewis base, weak O···H interactions can also play a role in the structure of the complex. Such secondary O···H interactions can also play a significant role in the structural arrangement between water and CO_2 molecules and thus in the solvation processes as it is for C−H···O hydrogen bonds in molecular recognition processes.[20,22]

Matrix isolation IR experiments[4,5] as well as high-resolution IR spectroscopy[3] and molecular beam electric resonance (MBER) measurements[6] in the gaseous phase suggest that the most stable structure of the H_2O−CO_2 complex is the planar T-shaped structure of C_{2v} symmetry for which the water protons point away from the CO_2 molecule with an O···C intermolecular distance of 2.836 Å. Moreover, microwave spectroscopy leads to a value of the internal rotation barrier of H_2O around its C_{2v} symmetry axis of about 0.86 ± 0.20 kcal/mol,[6] in close agreement with that reported by Block et al.[3] Nevertheless, some vibrational frequencies of the complex observed in matrix isolation spectroscopy have been interpreted as a possible signature of a secondary hydrogen-bonded H_2O−CO_2 complex.

Ab initio calculations provided quantitative characterizations of the properties of such CO_2 complexes. These calculations have shown that a binding energy of about −2.2 to −2.8 kcal/mol corresponds to the global energy minimum of the planar T-shaped structure. However, a local energy minimum has also been found corresponding to a complex having an almost H-bonded linear arrangement of the moieties with an intermolecular distance of 4.2−4.3 Å.[1] In this structure, the interaction energy is ranging from −1.2 to −1.6 kcal/mol.[2] Other possible structures of the complex have also been examined by Cox et al.[23] using the MP2/6-31G(d,p) level of calculations. Although this study confirmed that the planar C_{2v} structure (T-shaped) has the lowest binding energy, the authors argued that deeper quantitative study of the properties of these complexes needed more elaborate calculations to ensure a successful geometry optimization, particularly as the potential intermolecular energy surface (IPS) of the complex is very flat in the vicinity of the minimum. As a consequence, minor variations in the extension

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TABLE 1: Calculated Geometrical Parameters of the Optimized Structure of the H_2O-CO_2 Complex (C_s symmetry) at the MP2 Level of Perturbation Using Augmented Correlation-Consistent Polarized Valence Double/Triple Zeta Basis Sets[27−30] (The Binding Energy $\Delta E_{int}^{(cor)}$ (Corrected from BSSE) and the Electron Correlation Energy Are Also Reported with the BSSE and ZPE Contributions)

parameters[f]	aug-cc-pVTZ	aug-cc-pVDZ	binding energy[h,i]	aug-cc-pVTZ	aug-cc-pVDZ	literature
$d_{O_1H_2}$ (Å)	0.962 ($+1 \times 10^{-3}$)	0.966				
$d_{O_1H_3}$ (Å)	0.961	0.966				
α_{HOH} (deg)	104.6 (+0.5)	104.8 (+0.9)	$\Delta E_{int}^{(cor)}$	-2.6	-2.3	ΔE_{int}
$d_{C_4O_5}$ (Å)	1.170	1.180 ($+0.5 \times 10^{-3}$)				-6.2;[a] -8.0[b]
$d_{C_4O_6}$ (Å)	1.169 (-1×10^{-3})	1.179 (-1×10^{-3})	$\Delta E_{int}^{(BSSE)}$	$+0.2$	$+0.4$	-2.2; -2.4[c]
$\delta\alpha_{OCO}$ (deg)[g]	1.7	1.7				-1.9; -3.4[d]
R(C···O) (Å)	2.774	2.783	$\Delta E_{int}^{(MP2)}$	-0.7	-0.4	-2.2[e]
α (deg)	88.0	86.5				
β (deg)	139.6	146.8	$\Delta E_{int}^{(ZPE)}$	$+0.8$	$+0.8$	
ϕ (deg)	11.9	19.0				

[a] Reference 42. [b] Reference 12, SCF calculations. [c] References 2, 36, calculations at the MP2 level of theory with large basis sets. [d] Reference 1, MP2 and DFT-B3LYP calculations. [e] References 7, 23. [f] Significant angle and distance deviations from isolated CO_2 and H_2O monomers have been reported in parentheses. [g] $\delta\alpha_{OCO}$ indicates the bending angle deviation for CO_2 interacting with water. [h] Energy unit (kcal/mol). [i] $\Delta E_{int}^{(cor)}$, interaction energy corrected from the BSSE energy contribution $\Delta E_{int}^{(BSSE)}$; $\Delta E_{int}^{(MP2)}$ and $\Delta E_{int}^{(ZPE)}$, MP2 and zero-point energy contributions to the total binding energy, respectively.

of the basis set lead to significant differences in the distance associated with the complex energy minima.

Water solvation by liquid and SC CO_2 depends on a subtle balance between solute−solvent and solvent−solvent interactions. In condensed fluids, many-body interactions play a fundamental role in the solvation process. Nevertheless, theoretical chemistry can provide insights on the interaction energy of isolated pairs of solvent−solvent and solute−solvent molecules. Moreover, the influence of many-body interactions on both structure and stabilization energy of complexes formed by one water and two or three CO_2 molecules (trimers, tetramers) can also be assessed by ab initio calculations, and this constitutes a first step toward the understanding of the solvation mechanism.

This paper is aimed at the determination of the structures and binding energy values of the dimer and trimer formed between CO_2 and a single water molecule. The vibrational analysis of all of the structures investigated will be subsequently carried out using the standard Wilson FG matrix formalism.[24] Finally, the influence of cooperative O···H interactions with EDA forces on structures and spectral signatures of the CO_2 complexes formed with water will be discussed.

2. Methodology and Details of the Calculations

Ab initio calculations have been carried out using the Gaussian 98 program.[25] The structures of the water−CO_2 complexes and isolated moieties have been fully optimized at the second-order Moller−Plesset (MP2) level of perturbation theory[26] using a very tight criterion of convergence. The optimized structures and computed interaction energies of complexes have been achieved using the correlation-consistent polarized valence double cc-pVDZ and cc-pVTZ triple zeta basis sets, respectively,[27−29] augmented by diffuse functions (labeled using the prefix aug-).[30] The interaction energies (ΔE_{int}) have been calculated for the local energy minima structures and transition states of the water−CO_2 complexes. For dimer, the calculated binding energy has been corrected using the basis set superposition error (BSSE) by the full counterpoise (CP) technique.[31] For trimer, the BSSE corrected binding energy has been obtained according to the site−site function counterpoise method (SSFC).[32−35] In a second step, we have carried out a vibrational analysis of the water−CO_2 complexes using the standard Wilson FG matrix formalism[24] for the optimized structures and their individual moieties. In this framework, computed frequency values are assumed to correspond to harmonic vibrations.

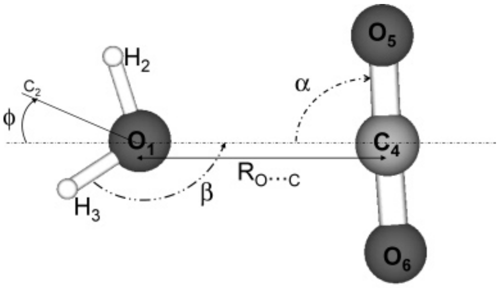

Figure 1. Optimized structure A (C_s symmetry) of the EDA CO_2 complex formed with water.

3. Water−CO_2 Complex

3.1. Structure and Binding Energy. At the MP2 level of the perturbation theory, using the augmented valence double and triple basis sets aug-cc-pV(D,T)Z level, the equilibrium geometry of the water−CO_2 dimer having the minimum value of the energy is a planar structure (labeled A) of C_s symmetry (Figure 1). The geometrical parameters of this optimized structure A are gathered in Table 1 and compared to those calculated for the isolated moieties. In this configuration, the electron donor O (oxygen)-atom of water interacts with the electron acceptor C(carbon)-atom of CO_2 with an intermolecular distance $R_{(C\cdots O)}$ ranging from 2.77 Å (VTZ) to 2.78 Å (VDZ) according to the augmented valence double and triple basis sets used. The hydrogen atoms of water are oriented in the opposite direction of the CO_2 molecule to minimize the overlap between orbitals of the O atoms of CO_2 with those of the lone pair of water. However, the ϕ angle (see Figure 1) varies from 11.9° (VTZ) to 19.0° (VDZ). The α_{HOH} angle of water interacting with CO_2 is slightly increased in comparison with that of isolated monomer (Table 1).

The BSSE corrected binding energy $\Delta E^{(cor)}$ ranges from -2.6 to -2.3 kcal/mol (Table 1). The electron correlation contributes to the interaction energy by about 20−30%. Taking into account the zero point energy (ZPE) correction, the calculated binding energy of this 1:1 complex is only of -1.5 to -1.8 kcal/mol. Even if experimental values of the interaction energy of this complex are lacking, our estimates are consistent with those predicted from structures reported in previous ab initio studies,[1−3,6,36] which are consistent with structures experimentally reported from matrix IR and MBER measurements.[3−5] Moreover, a few values of the binding energy available in the literature have been gathered in this table to be compared to

TABLE 2: Calculated Frequencies and IR and Raman Intensities of the $CO_2 \cdot H_2O$ Dimer in Optimized Structure[a]

	aug-cc-pVTZ			aug-cc-pVDZ			
	freq. ν (cm^{-1})	I_{IR} (km/mol)	I_{Ram} (Å^4/amu)	freq. ν (cm^{-1})	I_{IR} (km/mol)	I_{Ram} (Å^4/amu)	assignment
				Monomer H_2O			
ν_2	1628.4 (1195.4)	71.7 (36.36)	1.09 (0.60)	1622.3 (1190.7)	67.46 (36.11)	1.95 (1.03)	symmetric bending
ν_1	3821.9 (2764.1)	5.56 (4.34)	106.3 (55.56)	3803.3 (2751.2)	4.14 (3.39)	104.11 (54.59)	symmetric stretch
ν_3	3947.7 (2900.8)	75.46 (45.0)	22.8 (12.23)	3937.5 (2893.0)	67.02 (40.2)	24.18 (12.9)	antisymmetric stretch
				Monomer CO_2			
ν_2	659.0	22.64	inactive	655.5	21.46	inactive	degenerate bending OCO
ν_1	1325.8	inactive	33.47	1305.4	inactive	33.38	symmetric stretch OC
ν_3	2401.4	577.40	inactive	2379.2	567.59	inactive	antisymmetric stretch OC
				Dimer $CO_2 \cdot H_2O$			
	10.8 (8.8)	93.3 (71.1)	110.8 (106.5)	27.4 (22.5)	99.5 (75.8)	116.8 (111.8)	
	156.3 (112.3)	166.0 (147.5)		168.1 (124.3)	172.9 (149.7)		
	freq. ν (cm^{-1})	I_{IR}/I_{IR}°	I_{Ram}/I_{Ram}°	freq. ν (cm^{-1})	I_{IR}/I_{IR}°	I_{Ram}/I_{Ram}°	assignment, low-frequency modes (cm^{-1})
ν_2^1	648.8	1.66		646.6	1.66		in-plane bending
ν_2^2	662.6	0.97		657.8	0.98		out-of-plane bending
ν_1(CO)	1328.6		n.c.	1308.7		0.95	symmetric stretch OC
ν_2(HOH)	1626.5 (1194.8)	1.1 (1.2)	n.c.	1619.2 (1189.2)	1.2 (1.2)	0.75 (0.76)	symmetric bending
ν_3(CO)	2404.4	0.97		2383.2	0.96		antisymmetric stretch OC
ν_1(OH)	3818.5 (2761.4)	1.6 (1.6)	n.c.	3800.2 (2748.7)	1.65 (1.6)	0.97 (0.97)	symmetric stretch
ν_3(OH)	3944.6 (2899.0)	1.1 (1.1)	n.c.	3935.3 (2891.9)	1.1 (1.1)	1.1 (1.1)	antisymmetric stretch

[a] The intensity variations are normalized to the corresponding value of isolated monomers. The calculated frequencies and IR and Raman intensities of CO_2 and water monomers (MP2/aug-cc-pV(D,T)Z level) are also reported. The values reported in parentheses correspond to those obtained with heavy water (D_2O) in the complex.

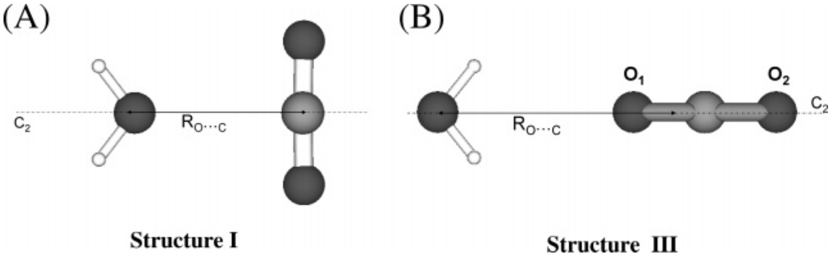

Figure 2. Structures of the transition states of the H_2O-CO_2 complex: (A) EDA structure I (C_{2v} symmetry), (B) structure III (C_{2v} symmetry).

our calculated values of the interaction energy. Even if Dunning's basis sets afford a convenient way to achieve a complete basis set (CBS) limit, our results are quite comparable to those obtained using Pople's basis sets,[1-3,36] and the BSSE contributions to the binding energy are of the same importance in both cases.

3.2. Vibrational Spectra. The computed harmonic frequencies, IR intensities, and Raman activities associated with the internal modes of the isolated molecules and the two moieties in structure A are reported in Table 2. We have also reported in this table the calculated low-frequency modes due to the complex formation for the different basis set considered. First, we consider the IR spectra associated with the ν_2 bending and ν_3 antisymmetric active stretching modes of CO_2, respectively. The EDA character of the interaction between water and CO_2 is established from the removal of the degeneracy of the ν_2 bending mode of CO_2, which leads to a doublet structure with a frequency splitting $\Delta\nu_2$ equal to 11.2 cm^{-1}. The first component of the doublet is assigned to the ν_2^1 in-plane mode of the perturbed OCO "bending" motion of CO_2 (in the plane formed by CO_2 and the O•••C intermolecular bond). It is situated at a lower frequency (∼646.6 cm^{-1}) than that of the isolated moiety (∼655.5 cm^{-1}), while its intensity is enhanced by a factor of 1.7 (Table 2). The second component of the doublet is assigned to the ν_2^2 out-of-plane mode (with reference to the bimolecular plane) associated with the perpendicular OCO "bending" motion of CO_2 and is located at a higher frequency (∼657.8 cm^{-1}) with an intensity slightly lowered. Upon complex formation, the ν_3 antisymmetric stretching mode of CO_2 is weakly shifted by 4.0 cm^{-1} toward higher wavenumbers, and its intensity is reduced by a factor of 0.96 as compared to that of the "free" CO_2. The ν_1 symmetric stretching mode of CO_2, inactive for the isolated molecule, exhibits now a weak activity and is slightly shifted by 3.3 cm^{-1} to higher frequencies. This mode, which is normally strongly active in Raman scattering, has its intensity slightly decreased by a factor of 0.96.

In this structure, the internal modes of water interacting with CO_2 are weakly perturbed (Table 2). Indeed, the ν_1 symmetric and ν_3 antisymmetric stretching modes are slightly shifted toward lower wavenumbers by 3.1 and 2.2 cm^{-1}, respectively. Their intensities are enhanced by 1.65 and 1.10 as compared to isolated water, whereas the Raman activities remain almost unchanged. The line position of the ν_2 bending mode of water is shifted toward lower frequencies by 3.1 cm^{-1}. In contrast to the OH stretching modes, the Raman activity of the bending mode is reduced by a factor 0.75, whereas the corresponding IR intensity is enhanced by 1.2.

3.3. Transition States. We found a first transition state of the complex with a planar T-shaped structure (labeled I) of C_{2v} symmetry (Figure 2A). In this configuration, the electron donor O-atom of water interacts with the electron acceptor C-atom of CO_2. The intermolecular distance $R_{(C\cdots O)}$ is 2.78 Å (MP2/aug-cc-pVDZ), and protons of water are symmetrically oriented in the opposite direction of the CO_2 molecule. The geometrical parameters of the optimized planar T-shaped structure are gathered in Table 3 for the basis sets used here. The BSSE

TABLE 3: Geometrical Parameters of the H_2O-CO_2 Dimer in Conformations I and III (Transition States of C_{2v} Symmetry) Calculated at the MP2/aug-cc-pV(D,T)Z Level[a]

	structure I		structure III	
variables	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVDZ
R(C···O) (Å)	2.773	2.777	4.382	4.385
d_{OH} (Å)	0.962	0.966	0.966	0.962
α_{HOH} (deg)	104.6	104.4	102.9	103.1
d_{OC} (Å)	1.170	1.180	(O_2C) 1.178 (O_1C) 1.181	(O_2C) 1.168 (O_1C) 1.172
$\delta\alpha_{OCO}$ (deg)[b]	1.8	1.7	0	0
$\Delta E_{int}^{(cor)c}$	−2.6	−2.3	−1.0	−0.9
$\Delta E_{int}^{(BSSE)c}$	+0.2	+0.7	+0.2	+0.4
$\Delta E_{int}^{(MP2)c}$	−0.7	−0.4	−0.4	−0.3

[a] The nomenclature of refs 7, 23 is used here to label the transient state of the H_2O-CO_2 dimer. [b] $\delta\alpha_{OCO}$ indicates the bending angle deviation for CO_2 in the 1:1 complex. [c] All energy values are given in kcal/mol.

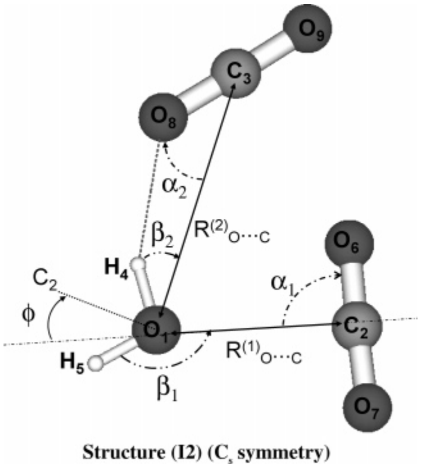

Figure 3. Optimized structure of the $H_2O-(CO_2)_2$ complex in the planar structure I2 (C_s symmetry).

corrected binding energy $\Delta E_{int}^{(cor)}$ is −2.3 to −2.6 kcal/mol using the valence double and triple basis sets, respectively (Table 3). The electron correlation and zero point energy contributions to the binding energy are also reported in this table. The more significant electron correlation contribution to the binding energy is obtained using the aug-cc-VTZ basis set with a value of −0.7 kcal/mol.

Another planar transition state of the 1:1 complex has been found in which the two water protons are situated at an equal intermolecular H···O distance of 2.71 Å (of 2.72 Å using the aug-cc-VTZ basis set) from the closest O_1-atom of the CO_2 molecule aligned along the C_2 symmetry axis (Figure 2B). Upon complex formation, the α_{HOH} angle of water is slightly decreased and the BSSE corrected binding energy $\Delta E_{int}^{(cor)}$ varies from −0.9 kcal/mol (aug-cc-pVDZ) to −1.0 kcal/mol (aug-cc-pVTZ) (Table 3). The two transition states (structures I and III) of the H_2O-CO_2 dimer are found with calculated binding energies that are in agreement with previous ab initio studies despite the dispersion of the calculated interaction energies due to basis size effects.

4. 1:2 Water−$(CO_2)_2$ Complex

4.1. Structure and Interaction Energy. At the MP2/aug-cc-pV(D,T)Z levels of calculations, we found a stable planar structure of the water−$(CO_2)_2$ trimer having C_s symmetry (Figure 3). The calculated structural parameters are gathered in Table 4. In this structure (labeled I2), the electron donor O-atom of water interacts with the acceptor C-atom of the closest CO_2 molecule situated at an interatomic distance $R_{(C\cdots O)}{}^1$ of about 2.76 Å. Both protons of water are almost pointed away from this nearest CO_2. This pair conformation appears as reminiscent of the structure A (in which $R_{(C\cdots O)} \approx 2.78$ Å, section 3.1) affected by the presence of a second neighboring CO_2 separated from water by an interatomic distance $R_{(C\cdots O)}{}^2$ of 3.82 Å (VTZ) to 3.84 Å (VDZ). The pair of CO_2 molecules interacts to form an oblique conformation characterized by a relative angle ranging from 63.0° (VDZ) to 79.1° (VTZ) between their highly symmetric axes. The intermolecular distance $R_{(C\cdots C)}$ is 4.0 Å. This orientational arrangement results from a subtle compromise between the “slipped” parallel geometry (C_{2h} symmetry) and the T-shaped structure (C_{2v} symmetry) found for the isolated CO_2-CO_2 dimer in previous studies.[37−41] A further examination of this structure shows that the arrangement between water and its second neighbor involves a second weak O···H−O hydrogen bond characterized by a distance of 2.13 Å (VTZ) to 2.15 Å (VDZ) due to the overlap between the lone pair of the O-atom of the farthest CO_2 molecule and proton of water. This interaction cooperatively acts with the main EDA interactions between water and CO_2.

For the equilibrium structure of the $H_2O-(CO_2)_2$ trimer, the interaction energy calculations explicitly include the irreducible three-body interaction contribution to the total interaction energy according to the site−site function counterpoise scheme:[32−35]

$$\Delta E_{int}{}^3(X,Y,Z) = [E(X,Y,Z) + E(X) + E(Y) + E(Z)] - [E(X,Y) + E(X,Z) + E(Y,Z)] \quad (1)$$

where, $E(X,Y,Z)$, is the energy of the (X,Y,Z) triplet calculated in the overall basis of the trimer, $E(X,Y)$ is the energy of the (X,Y) pair calculated in the overall basis of the trimer, and $E(X)$ is the energy of the X monomer calculated in the overall basis of the trimer.

The interaction energy (corrected from BSSE) of each (X,Y) pair in the trimer is given by:

$$\Delta E_{int}{}^2(X,Y) = [E(X,Y,Z) + E(Z)] - [E(X,Z) + E(Y,Z) + \Delta E_{int}{}^3(X,Y,Z)] \quad (2)$$

using for $\Delta E_{int}{}^3(X,Y,Z)$ the expression given in eq 1.

Using this generalized Boys−Bernardi scheme, the total interaction energy of the trimer (X,Y,Z) can be presented as the sum:

$$\Delta E_{tot}{}^{(SSFC)} = \Delta E_{int}{}^2(X,Y) + \Delta E_{int}{}^2(X,Z) + \Delta E_{int}{}^2(Y,Z) + \Delta E_{int}{}^3(X,Y,Z) \quad (3)$$

At the MP2/aug-cc-pV(D,T)Z level, the CP corrected total binding energy $\Delta E_{TOT}{}^{(SSFC)}$ of the trimer ranges from −5.1 to −5.8 kcal/mol (Table 4). The contribution to the total interaction energy due to the irreducible three-body term is −0.4 kcal/mol, that is, 7−8% of the total interaction energy. The electron correlation contribution is significant with a value of −3.4 kcal/mol amounting for 59−67% of the total interaction energy. The calculated interaction energy values of the water−CO_2 pairs in the 1:2 complex are, respectively, −2.6 and −1.7 kcal/mol (VTZ) and −2.3 and −1.6 kcal/mol using the VDZ basis set (Table 4). The remaining contribution to the binding energy due to the CO_2-CO_2 pair of molecules is −1.1 to −0.9 kcal/mol, a value comparable to previous binding energy estimates of the isolated dimer.[37−41]

TABLE 4: Calculated Geometrical Parameters of the Optimized Structure of the 1:2 $H_2O-(CO_2)_2$ Complex (C_s Symmetry) at the MP2/aug-cc-pV(D,T)Z Level[27−30] (The Binding Energy $\Delta E_{int}^{(cor)}$ Corrected from BSSE According to the Generalized Boys−Bernardi Scheme (See Text) and the Electron Correlation Energy (in Parentheses) Are Also Reported in This Table)

parameters[a]	aug-cc-pVTZ	aug-cc-pVDZ	binding energy[c]	aug-cc-pVTZ	aug-cc-pVDZ
$d_{O_1H_4}$ (Å)	0.964 ($+2 \times 10^{-3}$)	0.968 ($+2 \times 10^{-3}$)			
$d_{O_1H_5}$ (Å)	0.961	0.965 (-1×10^{-3})			
α_{HOH} (deg)	105.0 (+0.9)	104.7 (+0.8)	$\Delta E_{TOT}^{(SSFC)}$	−5.8 (−3.4)	−5.1 (−3.4)
$d_{C_2O_6}$ (Å)	1.172 ($+2 \times 10^{-3}$)	1.182 ($+1.5 \times 10^{-3}$)			
$d_{C_2O_7}$ (Å)	1.168 (-3×10^{-3})	1.177 (-3×10^{-3})	$\Delta E_{int}^{2}(1,2)$	−2.6 (−0.8)	−2.3 (−0.5)
$\delta\alpha_{OCO}^{1}$ (deg)[b]	1.1	1.9			
$d_{C_3O_8}$ (Å)	1.173 ($+2 \times 10^{-3}$)	1.182 ($+1.5 \times 10^{-3}$)	$\Delta E_{int}^{2}(1,3)$	−1.7 (−0.8)	−1.6 (−0.9)
$d_{C_3O_9}$ (Å)	1.167 (-4×10^{-3})	1.177 (-3×10^{-3})			
$\delta\alpha_{OCO}^{2}$ (deg)[b]	1.0	1.0	$\Delta E_{int}^{2}(2,3)$	−1.1 (−0.9)	−0.9 (−0.8)
$R_{(C\cdots O)}^{1}$ (Å)	2.755	2.764			
α_1 (deg)	85.5	86.9	$\Delta E_{int}^{3}(1,2,3)$	−0.4 (−0.8)	−0.4 (−1.5)
β_1 (deg)	151.2	151.2			
ϕ (deg)	23.7	23.6			
$R_{(C\cdots O)}^{2}$ (Å)	3.820	3.840			
α_2 (deg)	41.3	41.3			
β_2 (deg)	31.2	31.7			

[a] Significant angle and distance deviations from isolated CO_2 and H_2O monomers have been reported in parentheses. [b] $\delta\alpha_{OCO}$ indicates the bending angle deviation for CO_2 interacting with water. [c] Energy unit (kcal/mol).

TABLE 5: Frequencies and IR and Raman Intensities Variations of the $(CO_2)_2 \cdot H_2O$ Complex in Structure I2 Calculated at the MP2/aug-cc-pVDZ Level[a]

Low-Frequency Modes (cm^{-1})		
aug-cc-pVDZ		
18.9 (18.8)	31.6 (31.6)	68.6 (68.5)
71.3 (70.4)	91.2 (90.0)	119.7 (102.8)
137.9 (114.3)	141.3 (131.2)	243.5 (189.7)
354.5 (254.3)		

Internal Modes

freq.	symm.	ν (cm^{-1})	I_{IR}/I_{IR}°	I_{Ram}/I_{Ram}°
ν_2^1	A′	643.0	1.23	
ν_2^2	A′	650.2	1.99	
ν_2^3	A″	653.1	0.89	
ν_2^4	A″	657.3	1.07	
ν_1(CO)	A′	1310.6		0.59
ν_1(CO)	A′	1311.1		1.53
ν_2(HOH)	A′	1622.9	1.15	1.01
		(1191.0)	(1.17)	(1.23)
ν_3(CO)	A′	2385.8	1.10	
ν_3(CO)	A′	2387.3	0.97	
ν_1(OH)	A′	3789.5	11.35	1.30
		(2741.7)	(6.48)	(1.31)
ν_3(OH)	A′	3926.5	2.27	1.30
		(2885.0)	(2.14)	(1.23)

[a] The values reported in parentheses correspond to those obtained for heavy water (D_2O) in the complex.

In the equilibrium structure of the water−$(CO_2)_2$ trimer, a weak O···H−O interaction involving a proton of water cooperatively acts with the main stabilizing EDA interaction. It is noteworthy that such cooperative O···H−O hydrogen bonds are not unexpected as water interacting with CO_2 can act both as a Lewis base (sp^3 O-donating atom) and a Lewis acid (through protons of water). Thus, the weak O···H−O hydrogen bonds in the EDA complex formed between water and CO_2 play a significant role in the tuning of the inner structural arrangement of the trimer. Clearly, thorough structural investigations of 1:2 complexes provide better insight into mechanisms that should take place in condensed phase solvation.

4.2. Vibrational Spectra of the 1:2 Water−$(CO_2)_2$ Complex. We have reported in Table 5 the calculated harmonic frequencies (including low-frequency modes due to the complex formation), and the enhancement of IR and Raman intensities of the internal modes of water and CO_2 moieties in the equilibrium structure I2 (Figure 4). The use of the VTZ basis set at the (MP2) level of perturbation theory to determine the vibrational analysis of the trimer was precluded from calculations performed on the computers available by us. Therefore, the vibrational analysis of the trimer has been discussed in the following from calculations performed at the MP2/aug-cc-pVDZ level.

The main influence of the EDA intermolecular interactions between water and CO_2 is clearly put in evidence from the IR spectra associated with the ν_2 bending mode of CO_2 in structure I2. The removal of the degeneracy of the ν_2 bending mode leads to the formation of a quadruplet line structure with frequency values respectively situated at 643.0, 650.2, 653.1, and 657.3 cm^{-1}. In contrast with the 1:1 complexes, the ν_2^1 and ν_2^2 modes situated at the two lowest frequencies have to be assigned to a composite bending motion taking place in the σ-symmetry plane involving both CO_2 molecules (Figure 4). Thus, it should not be correct to assign in structure I2 the individual components of the multiplet as resulting from a degeneracy removal of the ν_2 mode associated with a particular CO_2 molecule in the complex. In contrast, the two lines observed at the highest frequency can be attributed more particularly to the weakly perturbed out-of-plane bending motions (i.e., perpendicularly to the σ-symmetry plane) of a particular CO_2 neighbor. The highest frequency ν_2^4 (657.3 cm^{-1}) mode originates from the high-frequency component of the split out-of-plane bending motion of CO_2, which mainly interacts with water in a quasi T-shaped configuration at a distance $R_{(O\cdots C)} \approx 2.764$ Å (Figure 4).The frequency of the ν_2^3 mode ($\sim$653.1 cm^{-1}) can be assigned to the out-of-plane bending motion of the second neighboring CO_2 molecule for which the doublet of split lines is globally shifted toward lower frequencies (Table 5).

In structure I2, the ν_3 stretching modes of both CO_2 molecules are shifted toward higher wavenumbers by 8.6 and 10.3 cm^{-1}, respectively. The line situated at lowest frequency is associated with the perturbed OC stretching motion of CO_2 interacting with water in a quasi T-shaped structure. The highest shifted line is associated with the perturbed OC stretching motions due to O···H interactions of the second neighboring CO_2 molecule with water. In the former case, the intensity of the ν_3 mode is increased by factor 1.10 as compared to that of “free” CO_2, whereas its intensity is decreased by a factor 0.97. The ν_1 stretching modes of the CO_2 molecules are shifted toward higher frequencies by 5.2 and 5.7 cm^{-1}. The Raman intensity of the symmetric OC stretch is also affected by interactions and increased by a factor of 1.15 as CO_2 interacts with water in a quasi T-shaped conformation. In contrast, the intensity is significantly lowered by a factor of 0.59 for the second CO_2 neighbor interacting also with water through a cooperative weak O···H−O interaction. The H-bonding character of this weak interaction is supported by both the red-shift and the IR intensity enhancement of the ν_1 and ν_3 stretching modes of water. The frequency of the ν_3 mode is lowered by 11.0 cm^{-1}, and its IR intensity is increased by 2.2. The spectral signature of this weak hydrogen-bonded interaction is more spectacular on the ν_1 mode of water, which is red-shifted by 13.8 cm^{-1} and for which the IR intensity is enhanced by 1 order of magnitude (Table 5). The Raman intensities of the two stretching modes are equally enhanced by a factor of 1.3. In contrast, the line position of the ν_2 bending mode of water is slightly shifted toward higher frequencies by 0.6 cm^{-1}, whereas its IR intensity is enhanced by a factor of 1.15 and the Raman activity is almost unchanged as compared to that of “free” water.

5. Discussion and Conclusion

Predictions reported here on the complex formation between water and CO_2 will be comparatively discussed with other EDA CO_2-complexes for which the base has an sp^3 O-donating atom (such as alcohols). A second issue will concern the influence of the CO_2−CO_2 and three-bodies interaction processes on structural and vibrational spectroscopic features of CO_2 complexes with water including at least two CO_2 molecules.

In this study, the calculated structure of the 1:1 complex is found rather consistent with that predicted in previous theoretical works, despite the relative dispersion on the binding energy evaluation due to the size and the quality of basis sets used in the literature.[1,2] At the MP2/aug-cc-pV(D,T)Z levels, the most stable structure A of the 1:1 complex is found planar (C_s symmetry) and mainly stabilized by EDA interactions. In this equilibrium structure A, the symmetry axis of water exhibits a slight tilt angle ϕ (ranging from 12° to 19°) as compared to the T-shaped structure (first transition state). However, no stable hydrogen-bonded structure has been found at this computational level.

The splitting of the ν_2 mode of CO_2 is strongly correlated with its arrangement in the complex. Clearly, the strongest perturbation due to EDA interactions is always experienced by the bending motion in the plane formed by CO_2 and the O···C intermolecular bond. This involves a significant shift of the $\nu_2{}^1$ mode toward lower wavenumbers together with an enhancement of the IR intensity by about a factor of 1.7. The $\nu_2{}^2$ mode associated with the out-of-plane bending motion is shifted toward higher wavenumbers with an almost unchanged intensity as compared to that of “free” CO_2. This leads to a frequency splitting $\Delta\nu_2$ of 12.1 cm^{-1}. This finding is utterly similar to results obtained from other EDA CO_2 complexes formed with sp^3-donor such as methanol and ethanol,[8] even if the frequency splitting is found to be greater at values of 16.4 and 17.1 cm^{-1}, respectively (binding energies of −2.95 and −2.97 kcal/mol). Underlying no hydrogen-bonding character due to O···H interactions, the calculated ratio $I_{IR}(\nu_1)/I_{IR}(\nu_3)$ of the IR intensity of the stretches of water is only found to be about 1.6−1.7.

For 1:2 complexes, the most stable structure I2 is formed with an additional CO_2 from a residual structure A of the dimer. This second neighbor reinforces the interaction energy of the primary water−CO_2 pair by −0.3 kcal/mol. The arrangement between water and this second neighbor results from a subtle competition between EDA interaction of the primary water−CO_2 pair, CO_2−CO_2 interactions, and weak O···H interactions (O···H distance of 2.15 Å) needed to stabilize the 1:2 entity. This can be also perceived through the attractive contribution to the binding energy of the irreducible three-bodies interactions (−0.4 kcal/mol).

For the 1:2 complex, the degeneracy of the ν_2 bending mode of CO_2 is removed to form quadruplet lines associated with a composed bending motion of CO_2 molecules interacting with water. That precludes us to interpret the spectral lines in terms of the individual internal mode of a molecule. However, the spectral analysis for the planar structure shows that the ν_2 modes situated at the lowest frequencies can be assigned with the in-plane “bending” motions perturbed by O···C interactions, whereas out-of-plane bending motions are rather situated at higher wavenumbers. Incidentally, our vibrational analysis confirms that generally the ν_1 and ν_3 stretches of CO_2 are found to be weakly perturbed (shifts, intensities) by interactions with water and CO_2 neighbors. This result was already shown for EDA CO_2 complexes formed with other sp^3-donors such as alcohols and sp^2-donor classes,[8−12] leading us to conclude that the OC stretches of CO_2 should not be suitable probes to provide unambiguously specific spectral signatures due to the EDA complex formation. The typical spectral signature due to cooperative O··H interactions between water and CO_2 in structure I2 is mainly observed from significant IR intensity variations and frequency shifts of the ν_1 and ν_3 modes of water. Incidentally, the ν_2 bending mode of water only exhibits slight shifts toward higher frequencies accompanied by weak IR intensity enhancement. Let us emphasize that the frequency shifts of stretching and bending modes calculated here for the trimer are in fair agreement with those measured for water highly diluted in SC CO_2 as a function of density.[15] This means that this kind of cooperative O··H interaction takes place in SC CO_2.

Finally, we conclude from our ab initio vibrational analysis that CO_2 complexes formed with water exhibit spectral signatures (frequency shifts and intensity variations) similar to those obtained of other sp^3-donors. More precisely, the ν_2 bending mode of CO_2 is strongly affected by interactions with water, whereas the CO stretches are more weakly perturbed. OH stretches of water suffer small frequency shifts and slight IR and Raman intensity variations by EDA interactions. Nevertheless, because water can play the role of Lewis base and acid as well, the existence (with O···C interactions) of secondary O···H interactions can introduce more pronounced spectral features associated with specific structures involving hydrogen bonding (structure I2).

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