Theoretical Study of the $CH_4{\cdot}(H_2O)_2$ and CH_4. $H_5O_2^+$ Complexes. Three-Hydrogen-Atoms Interaction

Eugene S. Kryachko[†] **and Thérèse Zeegers-Huyskens***

Department of Chemistry, University of Leuven, 200F Celestijnenlaan, B-3001 Leuven, Belgium

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The present work reports the results of the MP2/6-31+G(d,p) study of the interaction between CH_4 and $(H_2O)_2$ and $H_5O_2^+$, including the optimized geometries of the stable structures, their harmonic vibrational frequencies, total energies with the two- and three-body contributions, and natural charges. Three stable structures exist on the potential energy surface of the $CH_4{\cdot}(H_2O)_2$ complex formed via a CH···O hydrogen bond. Under its formation, the corresponding CH bond undergoes a small contraction, resulting in a blue shift of the corresponding ν(CH) vibration. One of the structures, resembling a cyclic trimer with relatively short distances between two hydrogen atoms of CH_4 and the terminal hydrogen atom of $(H_2O)_2$, is characterized by the largest total and the largest two-body interaction energies. This suggests the existence of a weak attractive interaction between the three hydrogen atoms. To shed light on the nature of such an interaction between three hydrogen atoms, we study the complex between CH_4 and $H_5O_2^+$ and demonstrate that its formation originates from a substantially stronger interaction between three hydrogen atoms and induces a marked asymmetry of the central (O···H···O) hydrogen bond of the cation. The distances between two hydrogen atoms of CH_4 and one of the terminal hydrogen atoms of $H_5O_2^+$ are very short (1.87 Å), implying that these three hydrogen atoms interact with each other due to a relatively strong ionic multi-dihydrogen bonding.

Introduction

It is well established that CH···O interactions play an important role in determining molecular conformations and crystal packing. Much of the evidence of such interactions stems from the observation of close H···O contacts in the crystal structure.[1,2] In the case of interactions involving C(sp) or C(sp^2) atoms, an elongation of the CH bond and a red shift of the corresponding stretching vibration have been observed. However, there is a rather limited number of cases where the CH···O interactions causes a contraction of the CH bond and a blue shift of the ν(CH) vibration.[3] One of them is the complex between methane and water.[4] It is worth mentioning that it has been recently shown that, in contrast to the CH bond of acetylene, the CH bond of methane shortens until the field reaches 0.02 au.[5]

The cooperativity is believed to be an important factor for the crystal strucure of compounds containing cocrystallized water molecules connected with CH···O hydrogen bonds.[6] Calculations carried out at the MP2/6-31G(d) level have shown that the nonadditivity correction in CH_4···O(H)H···B complexes (B being a nitrogen base) may rival or surpass the binding energy of the $CH_4{\cdot}H_2O$ binary complex.[7] To the best of our knowledge, there are no data available on the cooperativity in CH_4 complexed with proton acceptors. The present work aims to conduct a theoretical study of the interaction between CH_4 and the water dimer. We discuss the geometric changes, the interaction energies (including the two-and three-body terms), some selected vibrational frequencies and the charge shifts resulting from complex formation. The nature of the interaction in the complex formed between CH_4 and the $(H_5O_2)^+$ cation is also investigated and discussed.

Computational Methods

The geometries of the $CH_4{\cdot}(H_2O)_2$ complexes were optimized at the MP2/6-31+G(d,p) computational level. Harmonic vibrational frequencies were computed at the same level. Basis set superposition errors (BSSE) were taken into account by means of the counterpoise method.[8] Charges on individual atoms and populations of molecular orbitals (MOs) were obtained by using the natural bond population (NBO) scheme.[9] The GAUSSIAN 98 package of programs[10] was used for all calculations reported in the present work.

The total binding energy (E_{tot}) was evaluated as the difference in energy between the complexes, on one hand, and the sum of the energies of the isolated monomers, A, B, and C on the other hand, viz.

$$E_{tot} = E(ABC) - (E_A + E_B + E_C) \qquad (1)$$

This energy is then corrected via the counterpoise method by calculating the energy of each monomer in the basis set of all three subunits[11]

$$E_{tot}^{CP} = E(ABC) - [E_A(ABC) + E_B(ABC) + E_C(ABC)] \qquad (2)$$

The total two-body interaction energy E_2^{CP} in the ternary complexes was evaluated as the sum of the difference between the energy of a given interacting pair and the energy of the

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* Corresponding author. E-mail: therese.zeegers@chem.kuleuven.ac.be.

[†] On leave from Bogoliubov Institute for Theoretical Physics, Kiev, 03143 Ukraine. Present address: Department S13G, Limburgs Universitaire Centrum, Universitaire Campus, B-3590 Diepenbeek, Belgium. E-mail: eugene kryachko@luc.ac.be.

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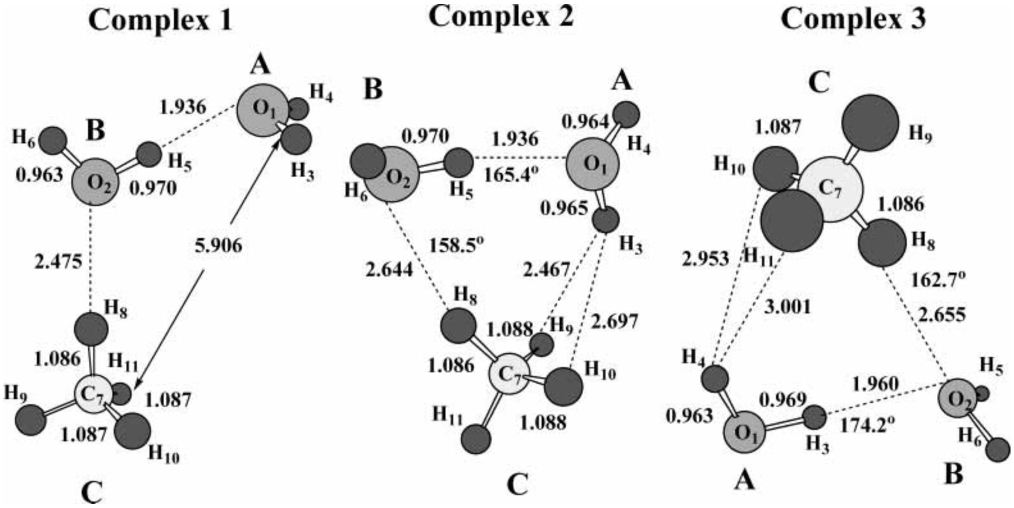

Figure 1. MP2/6-31+G(d,p) geometries (distances in Å, angles in degrees) of the three stable complexes **1**−**3** between CH_4 and $(H_2O)_2$.

corresponding isolated monomers, keeping all geometries frozen in the ternary complex structure,

$$E_2^{\mathrm{CP}} = E_{\mathrm{AB}}(\mathrm{ABC}) + E_{\mathrm{BC}}(\mathrm{ABC}) + E_{\mathrm{AC}}(\mathrm{ABC}) - 2[E_{\mathrm{A}}(\mathrm{ABC}) + 2E_{\mathrm{B}}(\mathrm{ABC}) + 2E_{\mathrm{C}}(\mathrm{ABC})] \quad (3)$$

The three-body nonadditive binding energy or cooperativity was obtained from the difference between the total energy and the two-body energy,

$$E_3^{\mathrm{CP}} = E_{\mathrm{coop}}^{\mathrm{CP}} = E_{\mathrm{tot}}^{\mathrm{CP}} - E_2^{\mathrm{CP}} \quad (4)$$

More sophisticated correlations, based on a perturbation scheme, have been proposed for a trimer.[12]

The 6-31+G(d,p) basis set was chosen to compare the present data with those related to the corresponding 1:1 complexes.[3e] For the $CH_4{\cdot}H_2O$ complex, the BSSE-corrected energy is rather insensitive to the computational methods including correlation effects.[3b] The same remark will certainly hold for the total two-body interaction energy and the three-body nonadditive energy, which are defined as differences (eqs 3 and 4).

Results and Discussion

Geometries of the $CH_4{\cdot}(H_2O)_2$ Complexes. The MP2/6-31+G(d,p) potential energy surface of the $CH_4{\cdot}(H_2O)_2$ interaction displayed in Figure 1 comprises three stable structures mirroring three different sites of the bonding of methane to the water dimer. In the first two structures, CH_4 is bonded to the two lone pairs (complex **1**) or to one of the two lone pairs (complex **2**) of the O2 atom of water molecule B. In complex **3**, the two lone pairs of water molecule B are involved in the interaction with CH_4 on one side and with water molecule A on the other side. Table 1 reports relevant geometric data in these complexes along with the corresponding parameters for the $CH_4{\cdot}H_2O$ complex and the $(H_2O)_2$ dimer, earlier calculated at the same level.[3e] It is also worth mentioning that complex **2** is less polar (its dipole moment is 2.7 D) than that of complexes **1** **(**3.4 D**)** and **3** (3.3 D).

We first start with discussing the CH8···O2 interaction between CH_4 and water molecule B in the ternary complex. In complex **1**, the CH8···O2 bond is nearly linear. The dihedral angle H8O2H5H6 is equal to −177°. This structure is analogous to one of the stable structures of the $CH_4{\cdot}H_2O$ complex where the CH8 bond bisects the lone pairs of oxygen.[4a] In complex **2**, the departure from the linearity of the CH8···O2 bond is much larger (21.5°) and the H8O2H5H6 angle is equal to 90.1°. This structure reveals similarities with the structure of the $CH_4{\cdot}H_2O$ complex reported in ref 4b where the approach of one of the lone pairs of the water molecule was thought to be preferential. In complex **3**, where the two lone pairs of water molecule B act as proton acceptor, the CH8···O2 bond also shows a relatively large departure from linearity (17.3°). The H8···O2 distance is shorter by ~0.17 Å than in structure **1** and also shorter by 0.03 Å compared to that in the $CH_4{\cdot}H_2O$ complex.[3e] In the three trimers, the interaction with the water dimer causes a contraction of the CH8 bond that is rather substantial in complexes **2** and **3**, (−0.14 mÅ in **1** vs −0.34 and −0.70 mÅ in **2** and **3**, respectively). Overall, this implies that the CH8···O2 hydrogen bond is stronger in complex **1** than in both the others. There are several reasons for that. The important one is that in **1**, CH_4 is simultaneously bonded to two lone pairs of water molecule B, which acts as the proton donor in the water dimer, in contrast to **2** where a single lone pair of B is involved and in contrast to **3** where B plays the role of the proton acceptor in the water dimer. This weakens its proton acceptor ability in forming the CH8···O2 bond. The other one is apparently that complexes **2** and **3** are cyclic due to a weak attraction between CH_4 and water molecule A which likely counteracts that between CH_4 and A. This suggestion will be further discussed.

TABLE 1: Relevant Geometric Data (Distances in Å, Angles and Dihedral Angles in Degrees), Variations of the Distances (mÅ) for the Three Stable $CH_4{\cdot}(H_2O)_2$ Complexes, and Corresponding Parameters for the $CH_4{\cdot}H_2O$ and $(H_2O)_2$ Dimers

	complex **1**	complex **2**	complex **3**	$CH_4{\cdot}H_2O$ or $(H_2O)_2$[a]
Δr(CH8)[b]	−0.14	−0.34	−0.70	−0.44
r(H8···O2)	2.475	2.644	2.655	2.507
∠C7H8O2	175.7	158.5	162.7	179.6
Δr(O2H5)[c]	7.3	7.3	6.2 (Δr(O1H3))	6.5
R(H5···O1)	1.936	1.936	1.960 (H3···O2)	1.946
∠O2H5O1	175.7	165.4	174.2	176.4
τH8O2H5H6	−177.0	90.1	−150.4	−180.0
τH5O1H3H4	129.4	130.7	126.3	126.3

[a] From ref 3e. [b] The CH distance in isolated CH_4 is 1.0862 Å. [c] The OH distance in isolated H_2O is 0.9631 Å.

Let us now analyze how the methane−water interaction along the CH8···O2 bond influences the initial geometry of the water dimer. As follows from Table 1, it undergoes only small changes. Compared with the free water dimer, the intermolecular distance between the two water moieties is shorter in complexes

TABLE 2: Total Interaction Energy for the $CH_4{\cdot}(H_2O)_2$ Complexes (E_{tot}), Two-Body (E_2) and Three-Body Contributions (E_3) (kcal mol^{-1}), and Percentage of Three-Body Contributions in Trimer Binding Energies (% Coop)

	complex **1**	complex **2**	complex **3**
E_{tot}[a]	5.24 (7.50)	5.55 (7.75)	5.09 (7.33)
E_2 (AB)[a]	4.76 (6.41)	4.73 (6.29)	4.79 (6.40)
E_2 (BC)[a]	0.26 (0.89)	0.23 (0.60)	0.31 (0.78)
E_2 (AC)[a]	0 (0)	0.29 (0.62)	0.12 (0.46)
E_2[a]	5.02 (7.30)	5.25 (7.51)	5.22 (7.64)
E_3[a]	0.22 (0.20)	0.30 (0.24)	−0.13 (−0.31)
% Coop	4.2 (2.7)	5.4 (3.1)	−2.6 (−4.2)

[a] The uncorrected-BSSE values are given in parentheses. All the energy parameters are calculated by eqs 1−4.

1 and **2** (both equal to 1.936 Å) and longer in complex **3** (1.960 Å). Such shortening parallels a slightly larger elongation of the O2H5 bond by 0.001 Å. In the three complexes, the dihedral angle H5O1H3H4 is almost the same, varying from 126.3° to 130.7°. However, the O2H···O1 bond in complex **2** rather strongly departs from linearity that is likely accounted for by the weak attraction between CH_4 and water molecule A.

As already mentioned, the structure of complex **2** resembles that of a cyclic trimer. The H3H10 and H3H9 distances are relatively short and equal to 2.467 and 2.697 Å, respectively. The O1H3 distance is sligthly more elongated (2 mÅ) than the O1H4 one (1 mÅ). This indicates the existence of a weak attractive interaction between the H3 atom, on one hand, and the H10 and H9 atoms, on the other hand. In complex **3**, the H4H10 and H4H11 distances are equal to 2.953 and 3.001 Å, respectively. These distances are markedly shorter than the H3H11 one of 5.906 Å in complex **1**. These weak interactions may also affect the total binding energies. This issue will be discussed in the next section.

Binding Energies and Cooperativities. Discussing the energetical features of the studied complexes $CH_4{\cdot}(H_2O)_2$, let us first notice that the BSSE-corrected interaction energy (excluding the ZPE-correction) in the binary $CH_4{\cdot}H_2O$ complex is equal to 0.29 kcal mol^{-1}. Notice also that the BSSE correction amounts 0.58 kJ mol^{-1}.[3e] The total interaction energies and their two- and three-body contributions in the three studied $CH_4{\cdot}(H_2O)_2$ complexes are collected in Table 2. The percentages of cooperativity defined as the ratio E_3/E_{tot} ($\times$100%) are given therein as well. Complex **2** has the largest total interaction energy. It is worth mentioning that the two-body interaction energy in the AC subcomplex is equal to zero in complex **1** and to 0.29 kcal mol^{-1} in complex **2**. The latter determines the two-body energy between the water molecule O1H3H4 and the CH9H10 group of methane. It is sligthly larger than the two-body energy between CH_4 and water molecule B (0.23 kcal mol^{-1}) and, on the other hand, it clearly indicates the existence of a weak attraction between the H3 atom of water molecule A and the H9 and H10 atoms of CH_4. It also exists in complex **3** though it is weaker by a factor of ∼2.5. The reason for such a difference is likely that water molecule A in complex **2** plays the acceptor role in water dimer AB whereas in **3** it is the proton donor. Interestingly, in both structures **1** and **2** where water molecule B acts as proton acceptor and proton donor, the BSSE-corrected cooperativities are equal to 4.2 and 5.4%, respectively, which is about half of the cooperativity in the open water trimer calculated at a comparable level[13a] (9.2%). Such a feature is rather unexpected in view of the substantially smaller proton donor ability of CH_4 as compared with that of H_2O. In contrast to **1** and **2**, the water molecule in complex **3** acts as a biacceptor. The three-body term and the resulting cooperativity then become negative (anticooperativity). It is worth mentioning that in the open water trimer, a large destabilizing effect takes place when the central H_2O molecule acts as a biacceptor.[13b]

TABLE 3: Frequency Shifts (cm^{-1}) of the ν(CH8), ν(O2H5), and δ(CH8) Vibrations, Intensities (km mol^{-1}) between Parentheses, Changes in Occupation of the σ*(CH8) and σ*(O2H5) Molecular Orbitals, Charge Transfers, and Changes in Natural Population of the C and H8 Atoms Relative to the Monomer (me)

	complex **1**	complex **2**	complex **3**	$CH_4{\cdot}H_2O$ or $(H_2O)_2$
Δν(CH8)[a]	+9 (1.1)	+4 (0.1)	+7 (3.1)	+12 (0)
Δν(O2H5)[b]	−170 (276)	−140 (339)	−120 (319) (O1H3)	−125 (370)
Δδ(CH8)[c]	+30 (6) +25 (6)	+25 (5) +19 (9)	+15 (9) +13 (6)	+27 (6) +19 (6)
Δσ*(CH8)	3.0	2.0	1.6	2.4
Δσ*(O2H5)	13.8	13.8	12.8 (O1H3)	13
CT[d]	2.8	2.3	1.7	2.3
Δq(H8)[e]	+33.6	+29.7	+15.1	+27
Δq(C)[e]	−9.4	−18.6	−10.2	−8

[a] ν(CH) in isolated CHD_3 = 3234 cm^{-1} (17 km mol^{-1}). [b] ν(OH) in isolated HOD = 3946 cm^{-1} (43 km mol^{-1}). [c] δ(CH) in isolated CHD_3 = 1354 cm^{-1} (5 km mol^{-1}). [d] Defined as the sum of the atomic charges on the water dimer. The last entry corresponds to the charge transfer in the $CH_4{\cdot}H_2O$ complex. [e] By convention, positive values indicate a loss of charge and negative values correspond to a gain of charge.

The present results may be also compared with data obtained on the cooperativity in the cyclic complex formed by formaldehyde and two H_2O molecules.[14] The CH bond length holds unchanged. However, the two-body binding energy for the CH···O interaction is equal to 2.1 kcal mol^{-1}. Thus, the two-body binding energies seem to be much larger for interactions involving C(sp^2)H than C(sp^3)H bonds.

Vibrational Frequencies and NBO Analysis. Table 3 reports the frequency shifts of some relevant vibrational modes along with the changes in occupation of the σ*(CH8) and σ*(O2H5) or σ*(O1H3) antibonding MOs. This table also includes the charge-transfer taking place from the $(H_2O)_2$ dimer to CH_4 together with the changes occurring in the natural population of the atoms C and H8 relative to the CH_4 monomer. By analogy with our previous work,[3e] the shifts of the ν(CH8) stretching vibration are calculated in the CHD_3 isotopomer to avoid a coupling with the other components of the $\nu^{as}(CH_3)$ vibration. For the same reason, the shifts of the ν(O2H5) vibration are calculated in the (D)O2H5···O2 isotopomers (complexes **1** and **2**) or D6O1H3···O2 isotopomer (complex **3**). Inspecting the data of Table 3, we conclude that in the three ternary complexes, the ν(CH8) is blue-shifted, by 4−9 cm^{-1}. There is no correlation between the contraction of the CH8 bond and the corresponding blue shift. Our findings are in agreement with calculations of ref 14, showing that cooperativy smoothly affects the vibrational properties of C(sp^3)H··· hydrogen bonds and that no clear trends in terms of red or blue shifts are observed.[14] A similar remark also holds for the intensity of the ν(CH8) vibration, which is equal to 17 km mol^{-1} in isolated CH_4, vanishes in the $CH_4{\cdot}H_2O$ complex, and becomes weak or even negligible in the ternary complexes. We also note a splitting and a blue shift of the degenerate deformation vibration, δ(CH8).

In the three ternary complexes, the occupation of the σ*(CH8) antibonding MO sligthly increases from its value in isolated CH_4. As could be anticipated from the cooperativity, the red shift of the ν(O2H5) vibration appears to be larger in complexes **1** and **2** and sligthly smaller in complex **3** than in $(H_2O)_2$. A stronger bonding between CH_4 and B in complex **1**, compared to $CH_4{\cdot}H_2O$ results in a shorter r(H8···O2) distance

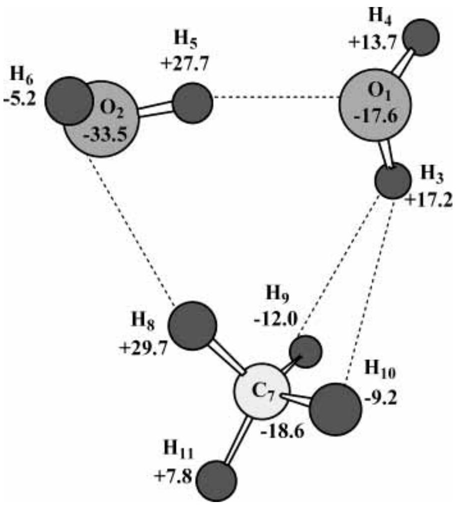

Figure 2. Charge shifts (me) in complex **2**. The sign + indicates a loss of charge and the sign − refers to a gain of charge with respect to isolated CH_4 and H_2O.

and in a larger red shift of the ν(O2H5) stretching vibration by 45 cm^{-1}. A smaller red shift of 15 cm^{-1} is due to the fact that the CH8···O2 bond is provided by a single lone pair of the oxygen atom O2. It is also worth noticing that in complex **2**, the ν(O1H3) vibration, calculated for the D4O1H3 isotopomer is red-shifted by 23 cm^{-1} and parallels a small elongation of the O1H3 bond. This shift is negligibly small for the other complexes and confirms the existence of the aforementioned weak attraction between the O1H3 bond and the C7H9 and C7H10 bonds discussed in the previous sections. Let us finally mention that the charge transfer, occurring from the $(H_2O)_2$ dimer to CH_4, and the increase in the occupation of the σ^*(CH8) and σ^*(O1H3) antibonding MOs take the smallest values for the anticooperative complex **3**. The change in natural population of the H8 atom is also the smallest for this complex. However, the change in the natural population of the C atom does not show a simple pattern, being the largest in complex **2** and approximately equal in **1** and **3**.

Nature of the Bonding in Complex 2. As concluded in the previous sections, complex **2** forms a cyclic trimer with a relatively large cooperativity due to two kinds of interaction. One of them is a weak CH8···O2 hydrogen bond, and the other one is the attraction between two hydrogen atoms H9 and H10 of CH_4 and the H3 atom of water molecule A. What is a type of such three-hydrogen-atom attraction to be referred to? The H3···H9 and H3···H10 distances, equal to 2.467 and 2.697 Å, respectively, are larger than the sum of the van der Waals radii of the hydrogen atoms (2.4 Å). The angles H3H9C7 and H3H10C7 are equal to 80.7° and 92.0°, respectively. Geometrically, such distances are larger than those inherent for the typical hydrogen bonds ($\leq$2.0 Å), although for some dihydrogen bonds[15] such as, e.g, in $ReH_5(PPh_3)_2$(imidazole), two distances (N)H···H(Re) markedly exceed 2.4 Å.[15b] The calculated values of the bond angles are essentially different from those existing in many theoretical quasi-linear dihydrogen bond complexes; however, they are rather close to those (90−120°) revealed from the experimental data.[15g−i] Energetically, the binding energy of such trihydrogen bonding is considerably lower, the typical ones of the dihydrogen bonding amounting to 4−6 kcal mol^{-1}.[15h]

To get a better insight onto the nature of such weak trihydrogen attractive interaction, the resultant charge shifts are evaluated using the NBO scheme and presented in Figure 2. Analyzing them, it appears that the interaction between CH_4 and water molecule A leads to a relatively substantial loss of the charge on H3 and increases it on the carbon and H9 and H10 atoms, together with its loss on H11. This shows first a rather strong shift of the atomic distribution in CH_4 resulting from its interaction with water molecule A, and second, a partial charge transfer of the charge from the O1H3 bond to the CH9 and CH10 ones. Therefore, concluding, there exists a clear-cut similarity between the present trihydrogen bonding and a subclass of weak dihydrogen ones that allows us to suggest that the former should be certainly referred to multiple dihydrogen bonds.[16] Complex **3** can also be viewed as partly formed by a weaker multiple dihydrogen bond. In both complexes **2** and **3**, the shifts in the atomic charge distribution on CH_4 results in their higher polarity, in comparison with complex **1**.

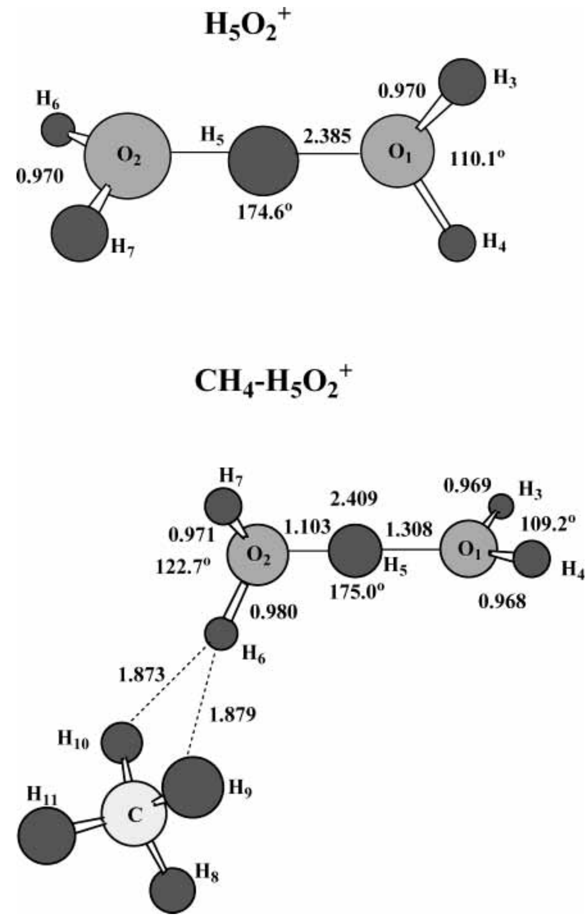

Figure 3. MP2/6-31+G(d,p) geometry (distances in Å, angles in degrees) of isolated $H_5O_2^+$ and the $CH_4.H_5O_2^+$ complex.

Interaction between CH_4 and $H_5O_2^+$. To demonstrate that the structure of complex **2** is not a specific feature of the $CH_4{\bullet}(H_2O)_2$ interaction, we investigate the interaction between CH_4 and $H_5O_2^+$, which is expected to be stronger. Its structure is displayed in Figure 3, which also shows the structure of the isolated $H_5O_2^+$ cation, useful for further comparison. The latter has C_2 symmetry, the O2H5 and O1H5 distances being both equal to 1.194 Å. This structure is in good agreement with the early data reported on this cation.[17] The harmonic ν^{as}(O1H5O2) vibration is predicted at 913 cm^{-1} with an infrared intensity of 2910 km mol^{-1}. The ν^{s}(O1H5O2) vibration calculated at 633 cm^{-1} is infrared inactive. The two deformation δ(O1H5O2) vibrations are predicted at 1524 and 1576 cm^{-1} with respective infrared intensities of 335 and 145 km mol^{-1}.

The structure of the $CH_4.H_5O_2^+$ complex shows interesting and rather unexpected features. We must at first notice the short intermolecular H6···H9 and H6···H10 distances, equal to 1.879 and 1.873 Å, respectively. These distances are shorter by 0.6−

0.8 Å than those in complex **2**. Interestingly, the interaction with CH_4 induces a marked asymmetry in the cation. The O2H5O1 bond remains almost linear, but the O2H5 and O1H5 distances become equal to 1.103 and 1.308 Å, respectively, indicating a marked shift by 0.09 Å of the middle proton toward O2. Also, the H6O2H7 angle increases from 110.1° in isolated $H_5O_2^+$ to 122.7° in the CH_4 complex. The interaction with CH_4 results in a marked elongation of 9.8 mÅ of the O2H6 bond. In contrast with complex **2**, the CH9 and CH10 bonds are elongated by 5.6 and 4.9 mÅ, respectively. The geometric changes parallel a shift of some vibrational modes. The ν(O2H6) vibration is red-shifted by 220 cm^{-1} and its infrared intensity increases by a factor of 5. The ν^{as}(CH9, CH10) and ν^{s}(CH9, CH10) vibrations become also red-shifted by 54 and 77 cm^{-1}, respectively. Strong perturbations of the vibrations involving the O1H5O2 part of the complex are also expected. Several vibrational modes are strongly mixed with the H3O1H4 and H6O2H7 deformation vibrations. This is the case for the modes calculated at 1430, 1668, and 1720 cm^{-1}. It is worth noticing that the mode predicted at 1905 cm^{-1} with an infrared intensity of 2440 km mol^{-1} involves predominantly the stretch of the O2H5 bond. Further, the mode calculated at 452 cm^{-1} has a predominant ν(O1H5) character. This mode becomes infrared active owing to the asymmetry induced by the interaction with CH_4. Its intensity takes a value of 145 km mol^{-1}. Our results show that the mode at 1905 cm^{-1} is shifted to higher frequencies by about 1000 cm^{-1} and the mode at 452 cm^{-1} is shifted to lower frequencies by about 180 cm^{-1} with respect to isolated $(H_5O_2)^+$. These results are in line with the contraction of the O2H5 bond, on one hand, and with the elongation of the O1H5 bond, one the other hand.

The interaction energy of CH_4 with $H_2O_5^+$ including the ZPE and the BSSE corrections amounts to 2.06 kcal mol^{-1}. This value is substantially larger than the two-body interaction energy E_{BC} in complex **2**. The charge-transfer taking place from CH_4 to the cation is equal to 14 me.

Let us now discuss the nature of the interaction between CH_4 and the studied cation. The H9···O2 and H10···O2 distances equal to 2.79 and 2.75 Å, respectively, are loo long to be categorized as true hydrogen bonds. Furthermore, the lone pairs are not correctly oriented and H6 lies in the middle of the bond. The H6···H9 and H6···H10 distances equal to 1.879 and 1.873 Å are sensibly shorter than the sum on the van der Waals radii. We may notice that similar distances have been calculated recently in dihydrogen bonds.[15f] However, the nature of the intermolecular interaction in the present complex differs from that inherent for dihydrogen bondings. Indeed, as discussed in the preceding section, all three involved hydrogen atoms being positively charged, cannot act as an electron donor. In the present case, the H9 and H10 atoms carry a positive charge of 0.20 e and the H6 atom a positive charge of 0.60 e. Furthermore, the interaction energy is much lower than in classical dihydrogen bonds. Indeed, for an intermolecular H···H distance of 1.87 Å, eq 1 of ref 15f allows one to predict the energy of 6.5 kcal mol^{-1}, which is nearly 3 times larger than the energy of the present complex. As previously discussed, the charge-transfer taking place from CH_4 to the cation is moderate and equal to 14 me. However, as illustrated in Figure 4, the studied interaction leads to significant charge shifts in both the electron-donor and electron-acceptor molecules. Our results indicate a polarization of the CH_4 molecule, the two terminal hydrogen atoms loosing 42 and 44 me, and the hydrogen atoms involved in the interaction gaining 15 and 26 me, respectively. There is also a loss of electronic charge of 39 me on the three H6, H7, and O2 atoms, an electronic charge of 54 me being removed to the terminal H3, H4 and O1 atoms. Summarizing, we may conclude that the $CH_4.H_5O_2^+$ complex is predominantly formed due to the ionic multiple dihydrogen bonding, by a straightforward analogy with the complexes treated in ref 16.

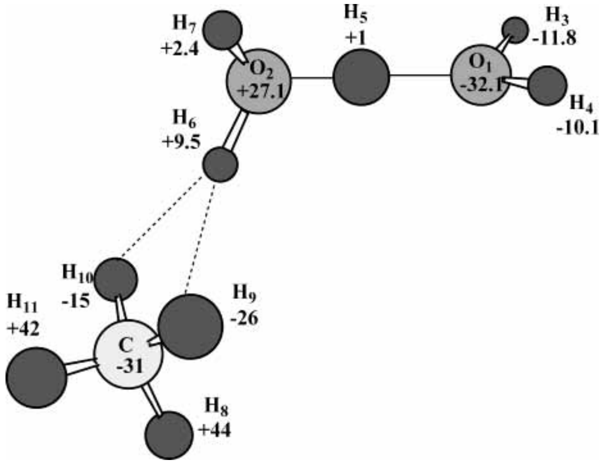

Figure 4. Charge shifts (me) in the $CH_4.H_5O_2^+$ complex with respect to isolated CH_4 and $H_5O_2^+$. The sign + indicates a loss of charge and the sign − refers to a gain of charge.

Conclusions

In this paper, we have reported a theoretical study of the interaction between CH_4 and the water dimer on one hand and the $H_5O_2^+$ cation on the other hand. In both cases, the most stable structure is stabililized by the attractive interaction involving three hydrogen atoms. This interaction differs from the classical dihydrogen bondings and may be considered as a type of multiple dihydrogen bonding.

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