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Geometrical and Electronic Structure of Hydrated CH_5^+ and CH_5^-

Pietro Cremaschi and Massimo Simonetta
C.N.R. Centre and Physical Chemistry Institute of the University, Milan

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Different conformations of isolated and solvated CH_5^+ and CH_5^- ions have been studied by CNDO method with Wiberg's parametrization. The anion has been found to have a most stable conformation of D_{3h} symmetry both in the gas phase and in solution. A C_s symmetry conformation is the most stable one for the isolated cation, whereas a conformation with C_{4v} symmetry is energetically preferred in solution.

Key word: CH_5^- and CH_5^+ ions, isolated and solvated ~

The structures of CH_5^+ and CH_5^- have been the subject of many theoretical investigations [1–9]. This interest among the theoreticians is justified by the fact that these ions can be used as models for the transition state in electrophilic and nucleophilic substitutions at alkanes and, on the other hand, they are not very suitable for experimental investigations. The most stable structures have been found to correspond to a C_s symmetry for CH_5^+ and D_{3h} for CH_5^-, both in semiempirical and *ab initio* calculations. When electron correlation is included [9] the difference in energy between the C_s and C_{2v} structures for CH_5^+ becomes negligible.

In all these calculations the two ions are supposed to be in gas phase, whereas the considered substitution reactions take place in liquid phase, where the influence of the packing of molecules of solvent around the ions could change the relative stabilities of the different conformations.

Following our more general purpose of studying the influence of the solvent on different physical properties [10, 11], in this paper we intend to perform theoretical calculations on a model system. The model was built by introducing directly around the CH_5^+ and CH_5^- ions several molecules of water in suitable positions, to reproduce the first shell of solvation. Owing to the large systems we are dealing with, we had to rely on a semiempirical method and the CNDO/2 method, with Wiberg's parametrization, has been chosen not only because for the isolated ions it gave results [2] in agreement with *ab initio* calculations [3, 9], but also because it was successfully used to study the influence of solvation on the energy barrier for $CH_3F + F^-$ reaction [10] and on blue and red shifts for $\pi^* \leftarrow n$,

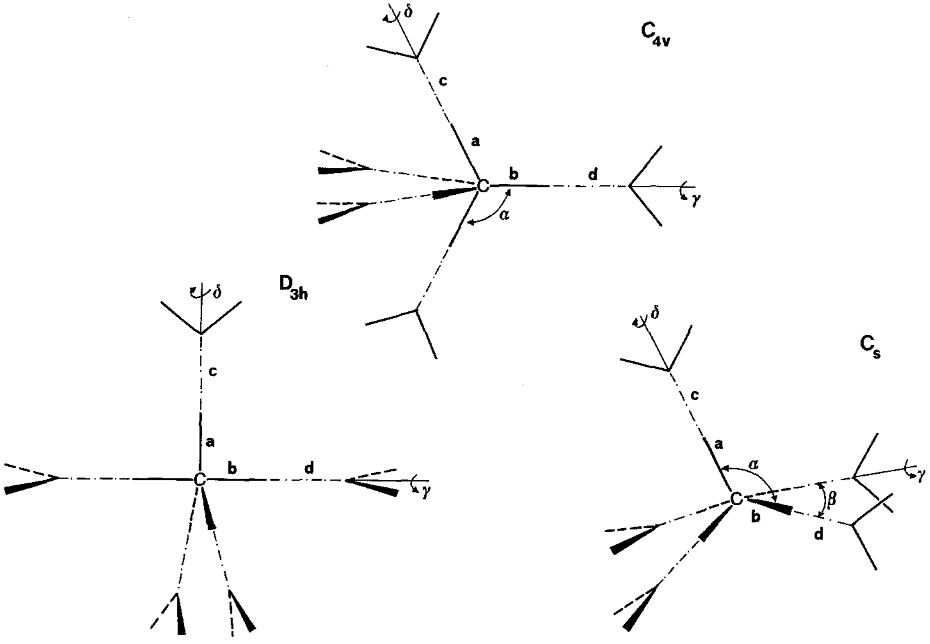

Fig. 1. Geometrical parameters for hydrated systems

$\pi^* \leftarrow \pi$ electronic transitions in a series of aldehydes, ketones and azines [11]. These previous results gave us some confidence both in the CNDO approximation and in the choice of the model.

The energies of the three different conformations taken into consideration (D_{3h}, C_{4v}, and C_s) were minimized by optimizing several geometrical parameters, using Powell's method [12].

A first calculation was made on isolated CH_5^- to determine its best conformation: a, b bond lengths and α, β angles (see Fig. 1) have been optimized; their values as well as total and stabilization energies, are shown in Table 1. D_{3h} structure has been found the most stable one. For the isolated CH_5^+ energies and geometries are taken from Ref. [2].

The optimized geometry of the isolated water molecule was found to be: $r(\text{O–H}) = 1.022$ Å, $\widehat{HOH} = 103.8°$ and its total energy $E_{\text{tot}} = -19.9281$ a.u.

To reduce the number of geometrical variables to optimize in the solvated systems, it has been assumed that the hydration shells reproduce the same D_{3h}, C_{4v}, and C_s symmetries of the isolated ions. The solvation shell has been simulated by five molecules of water along the directions of C–H bonds. A picture of the structures and variables to be optimized is shown in Fig. 1; corresponding numerical values, total and stabilization energies, and net charges are reported in Table 1.

In $(CH_5 + 5\,H_2O)^+$ the geometry of H_2O has been kept constant because the most stable structure has the oxygen atoms pointing to the hydrogens of the central ion, but in $(CH_5 + 5\,H_2O)^-$ $\widehat{HOH}$ angles have been optimized, as in the

Table 1. Optimized geometrical parameters[a, b] and energies of $(CH_5 + 5\ H_2O)^{\pm}$

	$(CH_5 + 5\ H_2O)^+$			$(CH_5 + 5\ H_2O)^-$		
	D_{3h}	C_{4v}	C_s	D_{3h}	C_{4v}	C_s
a(Å)	1.161 (1.14)	1.185 (1.16)	1.157 (1.14)	1.162 (1.162)	1.136 (1.138)	1.175 (1.175)
b(Å)	1.200 (1.16)	1.143 (1.13)	1.215 (1.21)	1.225 (1.225)	1.202 (1.201)	1.210 (1.209)
c(Å)	1.507	1.408	1.498	2.324	2.302	2.327
d(Å)	1.343	1.560	1.360	2.316	2.389	2.315
α(°)		110.3 (114.6)	113.1 (108.9)		103.9 (103.9)	120.7 (120.5)
β(°)			65.8 (50.0)			84.3 (84.3)
γ(°)	90.0	0.0[c]	0.0	90.0	0.0	0.0
δ(°)	0.0	0.0	0.0	0.0	0.0	0.0
ε(°)				101.3	101.2	98.2
E_{tot}(a.u.)	−109.9971 (− 10.1900)	−109.9984 (− 10.1980)	−109.9940 (− 10.2055)	−110.1206 (− 10.4354)	−110.1120 (− 10.4272)	−110.1006 (− 10.4156)
ΔE(Kcal/mol)	0.6 (10.0)	0.0 (5.0)	2.8 (0.0)	0.0 (0.0)	5.4 (5.2)	12.6 (12.4)
q_{CH_5}	+ 0.66	+ 0.68	+ 0.68	− 0.97	− 0.97	− 0.97

[a] See Fig. 1 for the symbols. ε is $\widehat{HOH}$ angle of H_2O.

[b] Values in brackets refer to isolated CH_5^+ (Ref. [2]) and CH_5^-.

[c] Free rotation.

Table 2. Optimized geometrical parameters[a] and energies of $(CH_5 + 10\ H_2O)^{\pm}$

	$(CH_5 + 10\ H_2O)^+$			$(CH_5 + 10\ H_2O)^-$		
	D_{3h}	C_{4v}	C_s	D_{3h}	C_{4v}	C_s
c(Å)	1.765	1.718	1.555	2.423	2.429	2.336
d(Å)	1.574	1.579	1.695	2.389	2.329	2.446
η(°)	70.0	83.4	76.0	73.6	71.0	89.6
ϑ(°)	80.0	78.8	82.6	77.4	90.0	80.8
E_{tot}(a.u.)	−209.6486	−209.6661	−209.6598	−209.8024	−209.7936	−209.7918
ΔE(Kcal/mol)	10.7	0.0	3.8	0.0	5.5	6.7
q_{CH_5}	+ 0.77	+ 0.75	+ 0.77	− 0.96	− 0.96	− 0.96

[a] See Fig. 1 and the test for the symbols.

structures of this system H_2O hydrogens are directed towards the anion. The opposite orientation has been found merely repulsive owing to negative charges on the oxygens and on the anion.

A larger model has also been considered in which the hydration shell is built of five couples of H_2O molecules, disposed along c and d directions, in such a way that the binary axis of the paired H_2O define η and ϑ angles, the bisectors of which are respectively c and d. Only the parameters c, d, η, and ϑ have been optimized, while for the remaining the values obtained in the corresponding calculations for $(CH_5 + 5\,H_2O)^{\pm}$ have been assumed.

By analyzing bond lengths and bond angles in Tables 1 and 2, it is evident that the molecules of the solvent interact more strongly with the cation than with the anion. In fact the optimized geometries of CH_5^- in gas phase and in solution are practically unchanged, while the differences between optimized geometries of CH_5^+ and $(CH_5)_{aq}^+$ are significant. The different interaction strength between the ions and the shell of solvent molecules is also outlined by the calculated electronic charges on the anion and the cation (Tables 1 and 2). Charge transfers from the anion to the surrounding water molecules are very small, only 0.03 and 0.04 for the two considered models of solvation, but higher charge transfers (0.32 and 0.23) have been found for the cation. On the contrary the ratio between the number of electrons on the carbon and that on the five bonded hydrogens, has been found always constant for the cation and the anion: 1.7 and 0.9 respectively.

Our results show that both in the model involving 5 and 10 water molecules the most stable conformation has C_{4v} symmetry for the cation, and D_{3h} symmetry for the anion. This means that while the conformation of the anion is preserved on going from gas phase to solution, the conformation of the cation is influenced by the surroundings, so that caution should be used when comparing the results of calculations performed for the isolated ion to experimental findings obtained in solution.

The overall impression is that for nucleophilic substitution we may expect configuration inversion to be a ground rule, while in electrophilic substitution we may find inversion or retention according to the medium in which the reaction occurs.

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Prof. Dr. M. Simonetta
Istituto di Chimica Fisica
Università di Milano
Via Golgi, 19
I-20133 Milano, Italy