



## Influence of Hydration on the Neutral Complex $(\text{OH}, \text{H}_3\text{O}^+)(\text{H}_2\text{O})_n$

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### ABSTRACT

Density-functional theory (DFT) within local density approximation (LDA) has been carried out for a sequence of hydrated proton clusters. Optimised structures were obtained for  $n=0, 1$  and  $3$  for  $(\text{OH}, \text{H}_3\text{O}^+)(\text{H}_2\text{O})_n$  complex. Hydronium ion  $\text{H}_3\text{O}^+$  and hydroxide ion  $\text{OH}^-$  are found to be the center of the neutral complex  $(\text{OH}, \text{H}_3\text{O}^+)$ . The LDA give shorter hydrogen bond lengths O-H, but slightly longer chemical bond lengths O...H as compared with the Post-Hartree-Fock calculations. We found that the distance O...H successively increases with the number of water molecules added to the neutral complex  $(\text{OH}, \text{H}_3\text{O}^+)$ . The solvent effects on proton transfer energy barriers in clusters have been studied. The harmonic vibrational frequencies and IR intensities of various modes have been generated for all optimised structures. This study was confirmed by vibrational studies of these complexes, our results give excellent agreement with experimental values.

**Key words:** hydrated proton clusters, density functional theory, the proton transfer, ab initio methode, intermolecular interactions, hydrogen bond.

### INTRODUCTION

The state of a proton in aqueous solution and clusters is of wide interest and the proton. Transfer reaction is one of the most important in chemistry<sup>1</sup>. Proton transfer also plays a very important role in biological processes<sup>2-5</sup>, however a proper description of such a process is still a major challenge for theoretical chemistry. Advances in theory and the availability of increased computer power have allowed substantial progress to be made for proton transfers in solution<sup>6-8</sup> and clusters<sup>9,10</sup>.

In recent months, the methods and techniques of density functional theory(DFT) have advanced remarkably<sup>11</sup>. They show considerable advantages of generality and accuracy with respect to the semiempirical methods and are more rapid than the highly correlated traditional ab initio methods that are required to treat questions of reactivity. They have been used to study small hydrated proton clusters  $\text{H}_2\text{O}^{+5}$ <sup>12,13</sup> and other hydrogen-bonded systems<sup>14</sup>. The energy barrier to proton transfer was calculated using<sup>12</sup> and compared with the results of other computational methods. A combined ab initio density functional

and classical molecular dynamics simulation (DFT CDFMD)<sup>15</sup> is under development to study quantum molecules in solution. It can be applied, in its present state, to calculate the free energy barriers of proton transfer in solution.

Small clusters provide a unique solvent environment, where reaction dynamics can be very different from that in aqueous solution. Recent advances in laser technology and molecular beam spectroscopy allow experimentalists to provide detailed information on the structure of the cluster. High resolution vibration-rotation spectroscopy of the hydrated hydronium ions, e.g.,  $H_5O^{+2}$ ,  $H_7O^{+3}$  and  $H_9O^{+4}$  have been obtained by Lee's group<sup>16</sup>. Many ab initio calculations have been published for  $H_5O^{+2}$ <sup>9,10,12</sup>. However, to our knowledge, except for some earlier results of Newton<sup>17</sup> and unpublished works of Remington and Schaefer<sup>18</sup>, very few ab initio results are available for the optimized structures and vibrational analyses for larger hydrated proton clusters.

In this paper, we report the ground state structures and the vibrational analysis for the hydrated proton the neutral complex  $(\cdot OH, H_3O^+)(H_2O)_n$  clusters with  $n=0,1$  and 3. Few of the methods used in ab initio are designed to probe the solvent effects on the energy barriers of proton transfer in the hydrated proton the neutral complex. The aim of our research is to study the effect of the interaction of several bodies on the structure of complex systems in the neutral  $(\cdot OH, H_3O^+)(H_2O)_n$ , with  $(n = 0, 1, 3)$ . These systems represent great interest in a chemical point of view in the biological field.

The study of these systems, it also provides information on the structure, the number of coordinate hydration and the nature of the routes to neutral complexes.

Our job is to study the properties of aqueous ionic solutions by ab initio calculations on the systems:  $(\cdot OH, H_3O^+)$  with symmetry  $C_1$ ,  $(\cdot OH, H_3O^+)(H_2O)$  with symmetry  $C_1$ ,  $(\cdot OH, H_3O^+)(H_2O)_3$ , with symmetry  $C_s$ . We will discuss three methods: Hartree-Fock, Moller Plesset perturbation, DFT with the 6-31 + G basis.

The remainder of this article is divided into three parts. The computational method is discussed in Sec.II, results are presented in Sec.III, and our conclusions are briefly summarized in Sec.IV.

### Computational Methods

We have computed the optimal geometries and harmonic vibrational frequencies of complex systems in the neutral  $(\cdot OH, H_3O^+)(H_2O)_n$ , with  $(n = 0, 1, 3)$ . A geometry was considered as optimized when the gradient was less than 0.0001 a.u.

All calculations were carried out in the ab initio<sup>19</sup> molecular orbital (MO) framework, using basis sets of contracted Gaussian-type orbitals (GTO's). The integral and SCF programs employed are those recently developed by Hehre and Pople<sup>20</sup>. We desired a basis set sufficiently flexible to give reasonable quantitative account of the structure and intermolecular energetics of the system under study while at the same time small enough so that a detailed study of potential energy surfaces of interest might be carried out economically. In preliminary minimal-basis calculations 6-31 + G<sup>\*\*27</sup> This includes polarization functions on all atoms with different levels; coherent self-field Hartree-Fock (HF)<sup>21</sup>, the perturbation method of Moller-Plesset (MP) to second order<sup>28-29</sup>, the density functional method (DFT)<sup>22-28</sup> calculations with the Perdew nonlocal corrections to exchange and correlation give somewhat shorter hydrogen bond lengths.

### RESULTS AND DISCUSSION

We studied the influence of hydration of the neutral complex  $(\cdot OH, H_3O^+)(H_2O)_n$ , by ab initio's calculation, with structural, vibrational, and energetic point of view. We started our study with the complex  $(\cdot OH, H_3O^+)$  which has a symmetry with the  $C_1$  complex then  $(\cdot OH, H_3O^+)(H_2O)$  with a  $C_1$  symmetry and the complex  $(\cdot OH, H_3O^+)(H_2O)_3$  which has a  $C_s$  symmetry, this study has been addressed by methods HF, MP2 and DFT / B3LYP with the 6-31 + G<sup>\*\*</sup>, all results are grouped in Tables (1,2,3,4).

The intra- and intermolecular coordinates complex  $(\cdot OH, H_3O^+)$  were optimized by three methods is (Table.1). The system stabilizes at a level of energy - 95426.04 kcal / mol by the HF

method, we notes in (Fig.1). The donor monomer ion  $H_3O^+$  has three covalent bonds, two bonds among them in the same plans, those formed by the oxygen atom  $O_1$  and the hydrogen atoms  $H_4, H_2$  which has a distance  $O_1-H_4$  and  $O_1-H_2$  equivalent to 0.944 Å. The route that is outside of the plan is formed by the  $O_1$  oxygen atom and the hydrogen atom  $H_3$  at a distance  $O_1-H_3$  of 0.963 Å. The angle  $O_1-H_3-H_4$  is 117.1 °, the angle of  $H_3-O_1-H_2$  is 114.8 °.  $^{\circ}H_2-H_4-O_1$  is 107.1 °, these three angles are closed to the angle 120°.

The donor monomer combined with the acceptor monomer OH by a  $O_5 \dots H_4$  hydrogen at a distance of 2.001 Å, which confirms that the three atoms  $O_1, O_5$  and  $H_4$  are in the same plane almost linear. A comparison of results with the values found in experimental observation hat the HF method is close to the experimental 0.04008% compared to the DFT method 0.04358% and the MP2 method 0.04226%.

The vibrational study of complexes with different methods HF, MP2 and DFT was made by the 6-31 + G \*\* basis, see (Table.2).

This table has been divided into two parts the first is the intermolecular vibration and the second intermolecular vibration. To explain this bungs have chosen the HF method, the appearance of three frequency bungs (137-630, 1743-1758, 4096-4257)  $Cm^{-1}$  of varying intensities (Table.2). The two first bungs correspond to intermolecular vibrations and the third bung

corresponds to the intermolecular vibrations, the frequency bung (4096-4257)  $Cm^{-1}$ , reply the OH stretch vibration, the band (1743-1758)  $Cm^{-1}$  is consistent with the deformation vibration (Bending), and the bung (137-630)  $Cm^{-1}$  corresponds to the intermolecular vibrations of the OH bridge linking hydrogen]. O-H..... O]. A comparison with experimental values 3385 and 3490  $Cm^{-1}$  reflects the values of frequencies calculated (Table2).

The next step, we add to this complex a water molecule to see the influence of the latter on the neutral complex ( $^{\cdot}OH, H_3O^+$ ). The system ( $^{\cdot}OH, H_3O^+$ )( $H_2O$ ) stabilizes with  $C_1$  symmetry, see (Fig. 2) at an energy level -143147.7 k cal / mol for the HF method see (Table 3). A comparison of results found with the experimental observation that in the HF method is closed to the experimental 0.04008 % compared to the DFT method 0.04358 % and the MP2 method 0.04226 %[30]. We noticed that there's a decrease of O-O distance of about 0.12 Å, and hydrogen bond distance of about 0.19 Å, there also a significant increase in binding of the  $^{\cdot}OH$  ion  $H_3O^+$  with a value of approximately 0.035 Å, and an increase in the angle of the ion of about 6 °even (Table 3).

The calculation of frequencies of vibration in these complexes restores the bung in the same frequency range, but with different intensities (Table.4) and the bung (277-870)  $Cm^{-1}$  corresponds to the intermolecular vibrations of the OH bridge linking hydrogen. O-H .....O., three (648,401, 617, 83, 583, 861)  $Cm^{-1}$  reply to the three hydrogen

**Table 1: The geometric parameters calculated at different levels of ( $^{\cdot}OH, H_3O^+$ ) and the comparison between results from experimental values**

Internal Coordinate	HF	MP2	DFT	Experiment <sup>a</sup>
$R(O_{(1)}-H_{(4)}), [\text{Å}]$	0.94417	0.9643	0.9658	0.950
$R(O_{(1)}-H_{(2)}), [\text{Å}]$	0.94423	0.9643	0.9658	0.950
$R(O_{(1)}-H_{(3)}), [\text{Å}]$	0.96353	0.97561	0.965859	0.950
$\psi(H_{(3)}-O_{(1)}-H_{(2)}), ^{\circ}$	114.8552	116.0936	113.1782	111.2
$\psi(H_{(1)}-O_{(4)}-H_{(5)}), ^{\circ}$	55.9870	55.2015	53.5312	-
$\psi(H_{(3)}-O_{(1)}-H_{(4)}), ^{\circ}$	117.13855	115.2018	112.3741	111.2
$\psi(H_{(2)}-O_{(1)}-H_{(4)}), ^{\circ}$	107.13855	105.679	106.0589	104.5
$R(O_{(5)}-H_{(6)}), [\text{Å}]$	0.94244	0.9624	0.9642	0.950
$R(O_{(5)}-H_{(4)}), [\text{Å}]$	2.001234	2.009184	1.923828	-

<sup>a</sup>Reference 30

Table 2: Harmonic vibration frequencies (in  $\text{Cm}^{-1}$ ) in the complex ( $\text{OH}, \text{H}_3\text{O}^+$ ) and experimental values the comparison between results from previous and experimental values

Inter molecular	System	MP2	HF	HF	DFT	DFT	Experiment <sup>a</sup>
		( $\text{cm}^{-1}$ )	( $\text{cm}^{-1}$ )	( $\text{cm}^{-1}$ )	( $\text{cm}^{-1}$ )	( $\text{cm}^{-1}$ )	( $\text{cm}^{-1}$ )
		IR Intensities (km/mol)	IR Intensities (km/mol)	IR Intensities (km/mol)	IR Intensities (km/mol)	IR Intensities (km/mol)	
$\omega_9(a'')$	Acceptor asymmetric O-H Stretch	4000.68	4257.29	4257.29	3924.24	86.8857	
$\omega_1(a')$	Donor free O-H Stretch	3978.55	4244.24	4244.24	3898.78	95.0156	3490
$\omega_2(a')$	Acceptor symmetric O-H Stretch	3861.32	4141.42	4141.42	3808.5	13.9001	3385
$\omega_3(a')$	Donor bridge H Stretch	3788.01	4096.08	4096.08	3696.96	332.356	
$\omega_4(a')$	$\text{H}_3\text{O}^+$ donor bend	1658.37	1758.94	1758.94	1631.95	46.8163	
$\omega_5(a')$	-OH acceptor bend	1636.92	1743.95	1743.95	1616.03	123.793	
$\omega_{10}(a'')$	H..(H-O-H) Out of plane donor bend	676.401	630.804	630.804	681.336	171.814	
$\omega_6(a')$	In- plane donor wag	372.019	359.79	359.79	393.602	97.2357	
$\omega_7(a')$	O-O stretch	202.215	186.384	186.384	205.659	198.959	
$\omega_8(a')$	Acceptor bend	178.67	167.948	167.948	179.521	35.652	
$\omega_{11}(a'')$	Acceptor twist	170.78	157.579	157.579	170.518	128.775	
$\omega_{12}(a'')$	Donor torsion	144.827	137.783	137.783	144.128	182.66	

<sup>a</sup>Reference 30

Table.3: internal study structure of the coordinate by taking into account the inter and intra-molecular interactions on the studied complexes

Intermolecular	HF		MP2		DFT		Experiment
	n=0	n=1	n=0	n=1	n=0	n=1	
R(O-O) [Å]	2.83405	2.8872	2.91435	2.79677	2.80547	2.78975	2.785082
R(O...H-O) [Å]	2.00123	2.0341	2.00918	1.9194	2.03678	1.8834	2.040007
<sup>a</sup> $\gamma$ (H-O...H)	55.9870	148.3984	55.2015	147.363	107.574	149.38	107.9534
<sup>b</sup> $\gamma$ (H-O-H) °	117.1385	91.679	115.201	91.6705	92.3665	90.951	97.15347
	107.1385	107.588	105.679	106.476	106.714	106.914	104.5 <sup>a</sup>
	114.8552	129.6005	116.093	127.810	131.338	124.22	111.2 <sup>a</sup>
R(O-H)c [Å]	0.94417	0.9508	0.9643	0.97561	0.98345	0.9801	0.950 <sup>a</sup>
	0.94423	0.9427	0.9643	0.97561	0.963	0.9643	1.017±0.005 <sup>b</sup>
	0.96353	0.9589	0.97123	0.9612	0.9749	0.983	1.01±0.01 <sup>c</sup>
R(O-H)d [Å]	0.94244	0.9424	0.96201	0.9627	0.9758	0.964	0.964 <sup>a</sup>

<sup>a</sup> Angle entre les deux ions  $\gamma$ (O-H...O)<sup>b</sup> Angle de lion  $H_3O^+$ <sup>c</sup> Distance de lion  $H_3O^+$ <sup>d</sup> Distance de lion  $OH^-$ <sup>a</sup>Reference **30**<sup>b</sup>Reference **31**<sup>c</sup>Reference **32**

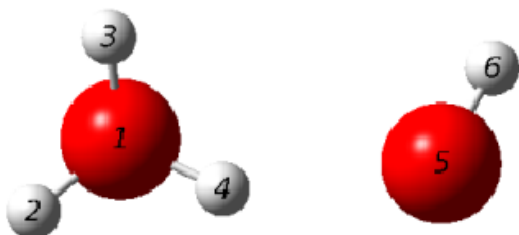
bonds of the appeared complex. By comparison with experimental values 3385 and 3490  $\text{Cm}^{-1}$ . We deduct, that the experimental values correlate well with the frequency values calculated for different levels in (Table.4). We recently added to the neutral complex ( $^-\text{OH}$ ,  $\text{H}_3\text{O}^+$ ) three water molecule to study the intra-and intermolecular interaction of the

system( $^-\text{OH}$ ,  $\text{H}_3\text{O}^+$ )( $\text{H}_2\text{O}$ )<sub>3</sub>, with an even symmetry  $\text{C}_s$  (Fig. 3), an energy level - 95933.46 kcal / mol for the HF method see (Table 3).The results are shown in Table 3 and Tables .4., A comparison with results found in the experimental observation ,also we notice that the DFT method is closed to the experimental 0.0152 % compared to the HF method

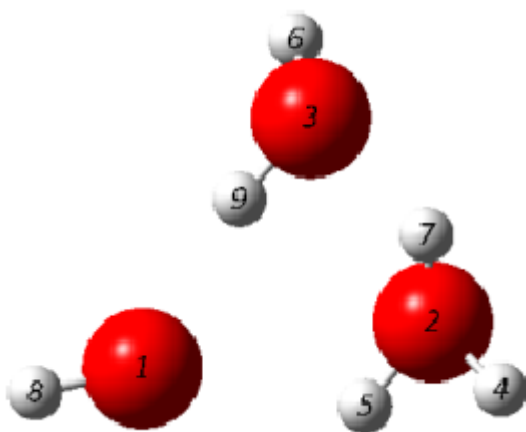
**Table 4: Harmonic vibration frequencies (in  $\text{Cm}^{-1}$ ) in the complex undermentioned and comparison between the experimental values**

System	MP2 ( $\text{cm}^{-1}$ )	MP2 IR Intensities ( $\text{km/mol}$ )	HF ( $\text{cm}^{-1}$ )	HF IR Intensities ( $\text{km/mol}$ )	DFT ( $\text{cm}^{-1}$ )	DFT IR Intensities ( $\text{km/mol}$ )	Expriment ( $\text{cm}^{-1}$ )	
( $^-\text{OH}$ , $\text{H}_3\text{O}^+$ )( $\text{H}_2\text{O}$ )	3969, 37	121, 161	4426, 65	946, 269	3899.19	57.2785	3490	
	3967, 98	111, 378	3980, 03	140, 362	3898.01	106.036	3385	
	3964, 63	110, 833	3945, 8	27, 3588	3893.22	97.4185		
	3730, 38	405, 507	3942, 27	93, 1109	3616.28	541.255		
	3722, 19	444, 006	3677, 15	633, 836	3603.68	596.1		
	1653, 42	116, 771	1828, 27	196, 862	1631.08	111.833		
	1649, 01	132, 572	1757, 69	74, 0879	1626.48	117.6		
	861.006	19.3183	915, 145	317, 613	912.853	16.1281		
	700, 657	455, 086	834, 851	319, 188	722.42	428.2		
	565, 813	179, 755	719, 518	53, 503	604.778	213.997		
	347, 639	124, 807	648.401	147.529	473.567	153.197		
	259, 698	42, 5834	617, 83	126, 958	380.,945	50.2188		
	210, 193	180, 261	583, 861	199, 244	270, 584	32, 195		
	192, 581	12, 1642	371, 754	55, 4202	250, 727	64, 5898		
	451, 07	150, 232	276, 676	8, 2816	177, 446	120, 171		
	( $^-\text{OH}$ , $\text{H}_3\text{O}^+$ )( $\text{H}_2\text{O}$ ) <sub>3</sub>	3775,99	693,479	423994	191,149	3896.98	60.5471	3025
		3722,56	143,642	4237,5	189,00	3895.4	130.992	2800
3712,24		627,636	4127,91	517,08	3894.05	126.164	2700 <sup>a</sup>	
3708,41		184,877	4063,3	453,999	3644.82	832.215	2600 <sup>a</sup>	
3667,24		287,406	4036,96	199,898	3597.31	535.396		
1651,57		143,642	1790,09	22,4773	3592.66	965.33		
1648,81		115,974	1751,9	174,096	1431,06	186,177		
897.157		29.0476	833.038	106.803	779.342	439.353		
760.545		412.5	811.627	4.2433	690.921	32.6021		
668.238		417.687	696.731	512.902	670.105	288.214		
641.291		24.0444	608.95	461.502	633..506	155.281		
598.752		267.709	566.166	19.4118	572.159	161.968		
404,899		115.238	534.352	263.968	430.787	25,2856		
380,691		162,138	473,519	142,43	416,043	145,337		
213,472		122,684	366,969	137,189	386,379	386.622		
226,801		165,693	205,617	70,304	270, 584	13,8428		
193,942		144,634	237,448	11,1279	250, 727	32, 195		
		180,813	67,7975	198,492	21,3725			

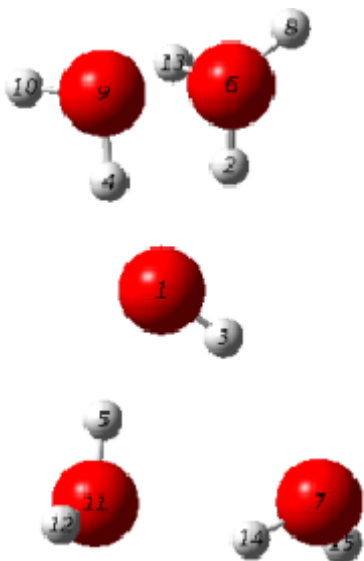
<sup>a</sup>Reference 33.



**Fig. 1: The neutral complex structure ( $\text{OH}, \text{H}_3\text{O}^+$ ) with  $C_1$  symmetry**



**Fig. 2: The neutral complex structure ( $\text{OH}, \text{H}_3\text{O}^+$ )( $\text{H}_2\text{O}$ ) with  $C_1$  symmetry**



**Fig. 3: The neutral complex structure ( $\text{OH}, \text{H}_3\text{O}^+$ )( $\text{H}_2\text{O}$ )<sub>3</sub> with  $C_S$  symmetry**

0.0215 % and the MP2 method of 0.0243 % . By varying the coordinat number there was a slight increase in distance R O-O 0.02 Å with a slight increase in hydrogen bonding distance of 0.21 Å. There is a decrease of O-H bond in relation to the first with a value of 0.01 Å, with a decrease of angle to the first with a value of 2 °. even .1,2,3 figures.

The calculation of frequencies of vibration in these complexes, gives a band (181-840)  $\text{Cm}^{-1}$  corresponds to the intermolecular vibrations of the O-H bridge linking hydrogen O-H .....O six frequencies (534.352- 566.166- 608.95- 696.731- 811.627-833.038)  $\text{Cm}^{-1}$  responds to the six hydrogen bonds of appeared complex. and other bungs frequencies in the same interval but with different intensities (Table. 4) that can be explained by the number of coordinat hydration and their positions (the symmetry of the complex), simply the influence of hydration has a great interest on the structure of the complex ( $\text{OH}, \text{H}_3\text{O}^+$ ) in comparison with experimental values 2700  $\text{Cm}^{-1}$  , 3025  $\text{Cm}^{-1}$  , 2600  $\text{Cm}^{-1}$  [33] and 2800  $\text{Cm}^{-1}$ , it is deduced that the experimental values correlate well with the values calculated for different frequency levels.

## CONCLUSION

A comparative structural and intra-and intermolecular energy by different levels MP2, HF, DFT with 6-31 + G \*\* basis on the neutral system ( $\text{OH}, \text{H}_3\text{O}^+$ )( $\text{H}_2\text{O}$ )<sub>n</sub>. The analysis of results has allowed us: to determine the configurations of coordinates that represent the complex neutral ( $\text{OH}, \text{H}_3\text{O}^+$ )( $\text{H}_2\text{O}$ )<sub>n</sub>. We notice that there is an important bonding increase of the  $\text{OH}, \text{H}_3\text{O}^+$  by adding water molecule in the complexe. In the comparative study of the hydrogen bond distance of a monomer to monomer donor acceptor complex in the neutral, we find that the distance O....H was reduced by the addition of three water molecules in complex and the energy gets weaker more and more by the addition of water molecule to the complex, it is predicted by the frequency of vibration.

We can conclude that this study has provided information on the structure, number of coordinat hydration and nature of the neutral complexes bonds, and our results give an excellent agreement with experimental values.

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