**Theoretical Study On Neutral Complexes M± (H2O) n**

**Preamble**

The present book that I am presenting entitled “**Theoretical Study on Neutral Complexes M± (H2O) n**” is more specifically intended for researchers, university students in the sciences of chemistry, physics and biology. It presents theoretical chemistry through a natural construction, starting from the principles of quantum mechanics.

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**General conclusion**

General Introduction

Solvation remains one of the most important questions in physics and chemistry.¶ The mechanisms for energy transport and molecular motion provide important clues to the structure and dynamics of solvation and lead to progress towards a detailed understanding of the influence of the liquid environment on chemical reactions. The behavior of aqueous gas-phase beams can provide insight into the hydrogen bonding nature of these neutral ion complexes.

The evolution of quantum theory, molecular dynamics, the performance of optimization algorithms and the availability of high-performance computer power have made it possible to simulate the description of the stability of ions in solution and at the level of complexes. Our theoretical study at different ab initio levels is based on optimizing and simulating the different systems studied. In predicts this evolution of energy by a representation of the potential of interaction for the modeling of these various systems.

The manuscript is presented in the form of three chapters, with an Introduction and a Conclusion.

In the first chapter, we approach Bibliographic study on the neutral complexes. The objective of this study is to present a certain number of reference and to give a definition hydration of the complexes. The latter represents a study on the binding and non-binding interaction in particular the cation binding to an anion present in water, with a description of the interactions, inter molecular and the force misses on games. One approaching the properties influence on the phenomenon of ionic solvation among them concentration, temperature and solubility.

The second chapter presents the field of our theoretical application: an overview on the modeling of systems; therefore a global approach on Calculation Methods. Our objective is on the one hand, to present a certain number of fundamental concepts on which we take support and on the other hand, to highlight the presentation of the various Algorithms of Minimization of the current systems.

We also approach the Different fields of force applied to an inter intramolecular system.

In the third chapter, we approach the calculations and results by studying the structural, energetic and vibrational aspect, on the application by calculations abinitio the Hatree-Fock method, the MP2 method and the DFT method, using the base 6-31G\*\* in different systems (-OH)(H2O)n , with (n = 0..5), (H3O+)(H2O)n with (n = 0..5), (H+)(H2O) n with (n = 0..5) and(-OH,H3O+)(H2O)n with (n = 0, 1, 3) , Finally this manuscript with a general conclusion which values our work.

**Chapter I. An overview of quantum physics**

**I.1 Introduction:**

The research and synthesis of new chemical and biochemical compounds are today often associated with a study by molecular modeling. Molecular modeling is a technique allowing not only to represent chemical properties and reactions but also to manipulate models of structures in two or three dimensions. The significant development in recent years of computer resources.

Has enabled chemistry to be enriched with computer tools specially dedicated to the representation of molecules. Thus, whether supercomputers or simple desktop computers, any chemist can today carry out a more or less exhaustive and precise study of molecular systems thanks to molecular modelling. The birth of more user-friendly software in recent years, the parallelization of computers, the appearance of Linux (LinusB.Torvald, 1991; an operating system similar to those of supercomputers but with a much lower purchase cost) have provided significant assistance in the development of molecular modeling.

ontrary to its beginnings, molecular modeling is now better recognized. In fact, in 1998, the Nobel Prize in Chemistry was awarded to John. A.Pople and Walter Kohn for their work in the fields of computational chemistry and molecular modeling (quantum chemistry). Also in 1992, Rudolph A.Marcus received the Nobel Prize For his theoretical work on the transfer of electrons, and in 1981, Kenichi Fukui, Roald Hoffmann received the same prize for their theoretical work on chemical reactions. When we use a particular model to predict the properties of a molecular system, we must be aware of the assumptions of the approximations implied by the model. Molecular modeling is used to simulate molecular systems, theoretical calculation methods such as quantum mechanics (QM) (ab initio or semi-empirical), molecular dynamics (DM), molecular mechanics (MM) and, for some years, the QM/MM association which seems very promising. In this chapter we present some concept of quantum mechanics.

**I.2** **The concept of quantum mechanics**

**a. Different approximations**

The principles of quantum mechanics cannot be implemented for systems representative of a phase because the calculation time is proportional at best to N electronHowever, their usefulness is real in molecular mechanics for the calculation of the interaction energy:

- to obtain the point atomic charges, involved in the calculation of the Colombian interactions.

-to obtain dipoles and other permanent multi-poles involved in the calculation of other electrostatic interactions.

- for the regression of the constants of recalls associated with the various vibratory modes of the molecules (elongation, bending, twisting).

Any system is considered in the form of nuclei around which electrons gravitate. Quantum mechanical calculations provide the nuclear and electronic properties of the system and the true total energy of the system. The total energy is related to the general wave function Ψ(r,t) dependent on coordinates and time by means of the generalized Schrödinger equation:

 (II.1)

Where H is the Hamiltonian, a mathematical operator describing the interactions of the system in the form of kinetic and potential contributions. Ψ(*r,t*) is interpreted as a presence probability amplitude and its square |Ψ(*r,t*)|2 is therefore the probability density of the presence of the particle, equal to unity when summed over all space.

If we assume that Ψ(*r,t*) can be written as the product of a function ψ*(r)* and H(t), t can be shown that the general Schrödinger equation breaks down into two equations, including the time-independent Schrödinger equation: (II.2)

his is the eigenvalue equation of the operator H. The possible energies are therefore the eigenvalues of H and the boundary conditions only allow E, the total energy of the system, to take only certain values (quantification).

This equation has an analytical solution for a one-electron system, i.e. for the single hydrogen H or helium atom He+. Any other system requires approximate techniques to be studied with an inevitable compromise between the desire to obtain results quickly and results with high precision.

We distinguish three main levels of approximation depending on whether we evaluate the interactions between the electrons more or less finely which lead to the following methods in increasing order of approximation:

*-* ab-initio (Hartree-Fock, CI)

- mean field (DFT Density Function Theory)

- semi-empirical

Among the ab-initio methods**[1]**, CI methods **[2]** (configuration interaction) are the ones that get the best results but are extremely slow. The energy values they calculate have a precision comparable to those generally measured experimentally. The solutions of IC methods are obtained by minimizing a linear combination of wave functions associated with the ground state of the system and all excited states. However, their application beyond a few tens of atoms becomes impossible even with a supercomputer.

For systems of a few hundred atoms, other approximations have been developed, including the model called Self Consistent Field Molecular Orbital (SCF-MO) **[3**]. It uses the concept of atomic orbital which represents the wave function of an electron moving within a potential generated by the nuclei and an average effective potential generated by the other electrons in the system.

The best wave functions of this type are calculated without any empirical parameters. They are called Hartree-Fock wave functions. **[4]** and solve the Schrödinger equation for a given electronic configuration (e.g. the ground state). They can then be used for CI calculations.

At the other end of the scale of approximations to SCF methods are the semi-empirical π electron models. Huckel's Molecular Orbital Theory **[5]** is the simplest. Finer semi-empirical models exist and make it possible to obtain with good precision ionization energies, optimal geometries with precise values of bond lengths and valence angles, potential energy surfaces. However, they have the disadvantage of not directly calculating the wave functions but trying to replace the different integrals with empirical parameters.

Between the two levels of approximation are the mean field methods including the popular density function theory DFT **[6-11]**.

**b. The generalized Hamiltonian and ab-initio methods**

 The goal of all numerical quantum mechanical methods is to determine the electronic structure of the system. For this, they must solve the Schrödinger equation in which the Hamiltonian operator H is equal to (the terms kernel – kernel are subject): (II.3)

Where: Zα is the atomic number and also the charge on the nucleus α, ri gives the position of the electron with respect to the origin, Rα is the position of the nucleus with respect to the origin, Δ2 is the Laplacian.

The summation over i and j refers to the electrons and the summation over α refers to the nuclei. The j > i avoids double counting the interactions between electrons.The term associated with the Laplacian is that of the kinetic energy of the electron cloud, the other two terms nucleus – electron and electron – electron being related to the potential energy.

The Hartree Fock method was the first to propose a way to solve the equation with the Hamiltonian of equation (II .3). For this, she uses the Born-Oppenheimer approximation which postulates that the nuclei being much heavier than the electrons, the latter instantly adjust to any movement of the nuclei or vice versa, that the nuclei appear fixed. Thus, one can separate the electronic and nuclear movements. The electronic wave function depends only on the positions of the nuclei and not on their kinetic energy.

Moreover, each multi-electron wave function ψ can be written as the product of mono-electronic wave functions φ. This implies that each electron moves in an average field due to the nuclei and other electrons. Cela caractérise ainsi les méthodes SCF.

In order to satisfy the Pauli exclusion principle **[12]**, ψ must be antisymmetric and we then write it in the form of a determinant, N!.

 (II.4)

The mono-electron wave functions i and the associated energies εi are calculated by solving N Schrödinger equations associated with each electron:

(II.5)

Where: VC is the Coulomb potential and VXi is the interaction exchange term which takes into account all the exchange terms between the electrons and host the interaction between an electron and itself. Then, an electron is subjected to a potential generated by all the other electrons and only them.

The solution wave functions of this equation can be expressed as approximate analytic functions called Slater orbitals **[13-17]** but it is an analytical Gaussian approximation of these orbitals that is most often used. According to the degree of Gaussian approximation, we get different ‘basis sets’. Thus the STO-3G basis means that a combination of three Gaussian functions is used to describe each atomic orbital. Names like 6-311++G(3df,3pd) or 6-311++G\*\* describe even more detailed bases **[15]**.

**c.** **Semi-empirical methods:**

Semi-empirical methods derive from Huckel's theory. The wave function φi is calculated as a linear combination of atomic orbitals χ:

 (II.6)

By substituting this expression in equation (II-5), we obtain: (II.7)

By multiplying by χμ and integrating over the whole space, we obtain:

 (II.8)

he semi-empirical methods consist in parametrizing hμν and Sμν to a greater or lesser extent.

****

Sμν is called the overlap integral. The energies εi are then determined by canceling the determinant of equation (II-8):

:



(II.9)

Then, each energy εi is substituted into equation (II-7) to determine the appropriate ciν coefficients used to reconstruct the mono-electron wave function φi by equation (II-9).

For the semi-empirical methods, the terms hμν and Sμν are replaced by empirical parameters in order to facilitate the resolution of the determinant of equation (II-7).

They give their name to the empirical methods: ZDO stands for Zero Differential Overlap (Sμν =0) **[18]**, MINDO Modified Intermediate Neglect of Differential Overlap**[19]**, … Among the most popular are AM1**[20-22]**, MINDO/3 **[23]**, MNDO, PM3**[24]** and MM2[**25].**

ll these methods are available through a large number of quantum mechanical calculation software packages (eg Hyperchem, GAUSSIAN**[26],** etc.).

d- **Théorie de la fonction de la densité :**

Solving the mono-electronic Schrödinger equation involves calculating countless integrals which de facto restrict the CI and Hartree-Fock methods to the study of small systems. Thus, the interactions between two electrons occupying two atomic orbitals φa and φb each connected to the positions of the two electrons involve the evaluation of 4 atomic orbitals. The calculation for a system with N electrons is therefore proportional to N4, i.e. 16,777,216 orbitals for 64 electrons!

However, Slater had the idea that "rather than trying to solve the Hartree-Fock exact problem in an approximate way, one could try to solve an approximate problem in an exact way". This amounts to modifying the Hamiltonian operator by replacing the correlation exchange term VXi with one of the main properties that can be deduced from the mono-electron wave function: the electron density ρi. The total electron density ρ gives an image of the electronic structure of the molecule. The electronic energy, εi is a functional of the electron density because each function ρi is associated with a unique energy (theorem of Hehenberg and Kohn).



(II.10)

For a system with N electrons, the resulting problem is then proportional to N2.

The precision of the results obtained with the density function theory presents an excellent compromise between the fast but coarse results of the semi-empirical methods and the precise but slow results of the most sophisticated ab-initio methods (the CI methods). Most current DFT applications **[27]** are based on the approach developed by Kohn and Sham, which uses single-electron functions (the Kohn-Sham orbitals). We therefore approach the Hartree-Fock method, namely that we use a fictitious system of independent electrons;

however, the electron density aims to be that of the correlated system. ρ (*r*) Is therefore written as the sum over all occupied KS orbitals:

 (II.11)

and the energy of the system is then:

(II.11)

The first term of this expression corresponds to the kinetic energy of the electrons; the second to the attraction between nuclei and electrons; the third reflects the Coulomb interaction between the charges and the last is a functional of the density and is called the exchange-correlation energy.

Obtaining the KS orbitals is done in a variational way, using an SCF type method.

**f. Basics of ab-initio calculation methods:**

The main current ab-initio calculation methods are based on the Hartree-Fock scheme with different series of bases.

They take into account all the electrons brought into play by each atom. Ab-initio methods provide rigorous and high-quality information on the properties of the molecule,

but they are very demanding in computation time and require powerful computers; also they are valid only for systems comprising a limited number of atoms.

The first bases used in intensive calculations relating to molecules polyatomic orbitals consisted of Slater atomic orbitals, denoted STO **[II.12].**



(II.12)

The exponents of the ξ orbitals (Zeta) must be chosen such that they correspond to a minimum of the energy, but this selection remains a difficult task even with computers because it leads to hard-to-compute integrals (multicentric integrals).

However, if instead of Slater orbitals we use bases in Gaussian functions, originally suggested by Boys in 1950 [13] **[28**] all multicentric integrals are very easy to calculate.

Hence the principle is the replacement, the latter is called an atomic Gaussian function (GTO) or Gaussian Type Orbital **[29]**. It has a very advantageous property [12] **[30]** ; the product of two Gaussians centered at two different points is equivalent to a single Gaussian. The use is currently made of the following bases: STO-nG (n = 2-6minimum basis where each Slater orbital is approximated by n Gaussian-like orbitals.

So, in the basis STO-3G each Slater OA is represented by three functions Gaussian.

In a database STO-6G, each atomic orbital is described by a sum of six Gaussian functions.

The base is said to be extended or with decoupled valence (split-valence) **[31]** [14], if each atomic orbital is represented by several functions. In the base N-nmG : N Gaussian functions describe the core orbitals, two functions describe the valence orbitals, one is of n fixed or internal Gaussian functions to describe the region close to the nucleus, the other of m free or external Gaussian functions for the more distant regions.

For example, a fashionable split-valence base widely used in calculations in theoretical chemistry is base 6-31G.

Consider a carbon atom in the base 6-31G; the 6 indicates that the 1S orbital of the carbon atom (the orbital representing the inner shell) is described by a sum of six Gaussian functions, the 2S and 2P orbitals described by three fixed (internal) Gaussian functions and one free (external) **[32].**

The polarized bases take into account the outermost unoccupied atomic orbitals in the ground state of the atoms. These atomic orbitals are also described by Gaussian functions.

Adding an asterisk \* in superscript (e.g. 6-31G\* or 6-31G(d)) indicates that one is adding a single set of 3d Gaussian functions to the split-valence basis for the description of heavy atoms .

A double asterisk \*\* (for example 6-31G\*\* or 6-31G (p, d)) means that in addition to the 3d OAs, we add to the split-valence basis a single set of 2p Gaussian functions for the description hydrogen atoms **[33].**

**I. 3 Conclusion:**

The use of molecular modeling should therefore not be considered as a black box in which we enter an initial state and which in return gives a final state. It is above all a simulation work that requires in-depth knowledge of the system studied, but above all a good understanding of the representation models used.

**Chapter II. Study Bibliography on neutral complexes**

**II .1- Introduction :**

Structural and energy studies of ionic complexes are very important in the field of biology, pharmacy and chemistry, allow us to understand the phenomena of solvation in solution **[1-3]**. ¶¶ Theoretically, the molecular simulation of the complexes has been carried out by several researchers **[4-6],** such studies provide insight into the structure and energy of neutral ion complexes. ¶ The hydration of hydronium ions is of great interest for chemistry, [7] not only for their presence in the ionosphere **[8],** but because they govern the process of proton transfer in aqueous solutions **[9-10]**.

The hydronium ion is three times donor and the hydroxide ion is once acceptor or donor of the proton. In this first chapter we present a bibliographic study of the structural properties, energy, as well as a dynamic study of ionic complexes in water. In addition, we will focus on the intermolecular interactions involved in these systems. First, a definition of the hydronium ion **H3O+** and the hydrate ion **HO-**  in the gas phase and in aqueous solution is presented. Secondly, we approach the phenomenon of the hydration of H3O+ and HO- ions in water, and give an overview of the structure of the ion which is located in the center of the complex surrounded by water molecules in the cluster thus formed. Third, a comparative analysis of the hydration **M± (H2O)n ,** presented, where M represents different transition metals and the alkali metals.

Fourthly, a definition of Complexes is given with an overview of some recent bibliographical studies. In conclusion, we highlight the importance of these ionic complexes in the different scientific fields.

**II.2- hydronium ion H3O+:**

**a. Hydronium Ion Definition (H3O+):**

The oxonium ion is found in the non-hydrated state in solid substances and crystalline compounds. In contrast, the hydronium ion exists only in aqueous solution. It is then surrounded by several molecules of water (H2O) n in indeterminate number (which therefore does not strictly make it a chemical complex) with which it maintains hydrogen bonds. Hydronium ion existing in aqueous medium; it is a hydrated oxonium ion, informally surrounded by several layers of water molecules. The polar water molecules are bound around the positively charged oxonium ion, under the influence of weak electrostatic forces. This phenomenon called solvation or solvent interaction is called hydration in water.

### Solvent water The hydronium ion is permanently present in water, due to the autoprotolysis reaction. First there is dissociation of a water molecule.


H_{2}O \leftrightarrow H^{+} + HO^{-} 
. (I.1)

Then a second molecule of water gives a complex with the proton obtained.
H_{2}O + H^{+}\rightarrow  H_3O^{+} 
 (I.2)

The overall reaction scheme can be written:


2H_{2}O \leftrightarrow H_{3}O^{+}_{(aq)} + HO^{-}_{(aq)} 
 (I.3)

HO-(aq) being the hydroxide ion which is also subject to the phenomenon of solvation..

evertheless, this reaction is of little importance since in pure water, at25°C, only **10-7** mole of water has dissociated per liter of water.

The hydronium ion is responsible for the property of acids according to Bronsted's definition. It is present in all aqueous solutions in equilibrium with the hydroxide ion HO-. t is the measurement of its concentration that makes it possible to determine the pH of the solution.

Some studies show that the hydronium ion **H3O+** in aqueous solution has a symmetry **C3V** and has a pyramidal structure. This configuration was obtained by Diercksen et al. **[11]** using the HF method with bases containing polarization functions. The geometric parameters obtained are an **O-H** distance of **0, 972** **Å** and a bond angle of **113,55°.**

**II.3-** Hydroxide ion **HO-:**

**a.** Definition of hydrate ion **HO- :**

It is formerly noted –OH the first writing makes it possible to highlight the fact that the negative charge is carried by oxygen. Chemically, it is a base but also a nucleophile. Its basic character is measured by an equilibrium constant while its nucleophilicity is measured by a rate constantt is one of the simplest polyatomic ions. The term “hydroxide” can also designate any single containing a stoichiometric quantity of this polyatomic ion.

The hydroxide ion **HO-** is unstable, and its lifetime is of the same order of magnitude as that of the hydronium ion **[12].** The inter-atomic distance determined in the gas phase **[13]** is equal to 0.964 Å, it is close to the results obtained by IKUTA **[14]** who optimized the O-H distance, using the SCF MO method with the two bases 6-31G\* and 6-31+G\*. These values are respectively: 0.963 Å and 0.956 Å. Avec la même méthode **SCF MO** mais des bases de fonction gaussienne différentes **6-311 G\*\*** et **6-311 G\*\*+p,** **G. Andoloro** et **al [15]** ont minimisé l'énergie de l'ion hydroxyde **HO-** qui vaut **-76.360 Hartree** avec une longueurde liaison **O-H** égale à **0, 97 Å.**

### II.4- Hydration of H3O+ (H2O) n  and HO-(H2O) n :

In biological or chemical environments, polar molecules, more precisely those which are ionized, are surrounded by water molecules. Positively charged molecules interact with the oxygen atom of water and negatively charged molecules with the hydrogen atom. It is assumed that when two hydrated molecules interact, they "dehydrate" at least partially before and during their interaction. These low-energy interactions, which are observed in particular between messengers (donors) and receptors (acceptors), are generally reversible.

**Andrew T.Pudzianowski [16]** deepened his research by studying the **H3O+/ H2O** system with the same 6-311++G (d, p) at the MP2 and HF levels.

From these results, he was able to conclude that the MP2 method, with the low 6-311++G (d, p) better minimizes the energy compared to the HF method and gives an enthalpy value closer to the ΔH (K cal / mol) =-35, 0.**[17].**

The lifetime of **H3O+** in aqueous solutions has been estimated to be ten times longer than the duration of molecular vibrations **[18-19]**

The hydronium ion is hydrated by four water molecules in the first solvation shell **[17].**

Among these molecules three are linked by hydrogen bonds **O-H……O** and the fourth through a charge-dipole interaction **O+…………H/2O.** Both types of interaction play an important role in the stability of these configurations .

Andrew T.Pudzianowski [20] thus studied the **HO-/ H2O** system with the same base 6-311++G (d, p) as well as the two **MP2** and **HF** methods but giving, in addition, the physical properties like ΔH (Enthalpie en kcal / mol), ΔS (Entropie en cal/ mol. K), ΔG (cal).

He noted that the **MP2** method, with the base 6-311++G (d, p) minimizes the energy better than the **HF** method and gives an enthalpy value closer to the experimental ΔH (K cal / mol) =-27, 0.**[21]**

The **HO-/H2O** geometry has been the subject of various works **[22-24] ; Roos, Kramer and Dierksen [23]** optimized the system by the HF method using an extended 6-311+G (d, p). They confirm that the planar asymmetric configuration is more stable than the symmetric configuration with an energy difference of **1, 58 KCal/Mole.** These results are proven by ab initio calculations presented by Bernard Schlegal **[20].**

Nevertheless the number of water molecules of hydration of the hydroxyl ion remains controversial. Newton and Al  **[24]** demonstrated that the first layer is formed of three water molecules, the same results were obtained by Daniel Rinaldi **[23]** whereas M. Tuckerman

**[25]** shows the existence of four molecules in the first solvation shell.

Recent experimental and theoretical studies carried out on aqueous beams show the behavior that characterizes these systems **[26-36].** Experimental work that indicates that water structures with well-defined geometry hardly cage ion, such as H3O + **[30-31]**, OH- **[32]**. This study considered 20 molecules of water surrounded by the central ion. They deduced that the stability increased with the number of water molecules added.

**¶Lin [37]** c’est he was the first to study the discontinuous mass-spectral distribution for H3O+ (H2O)n, ¶ beams, produced by water vapor ionization. Similar behavior has been observed to protonate water beams under a wide variety of experimental conditions **[38-48]** .

¶ heoretical and computational methods were employed to precisely study the structure and energetics of the clusters **[45,49-57]**, some of these studies have indicated that the magic number of the group H3O+(H2O)20 **[45,53]** and NH4+(H2O)20 **[49]** are energetically similar sizes, although the original structure and the statistical reliability of the calculated effects is not the same. A more recent calculation by Kozack and Jordan using the fully polarizable interaction model, which confirms the relative stabilities, of H3O+(H2O)20 and ¶H3O+(H2O)19 are comparable **[56].**

In 1970, several frequency studies by ab initio calculations of the free -OH ion and HO-….(H2O)n systems with (n≤4) **[58-60]** **Lischka, [80]Lischka, Carsky and Zahradnik**, **[81]** ¶and **Spirko, Kraemer, et Cejchan** **[60]** .

¶ **¶Skogby and Rossman**, **[61]** studied the incorporation mechanisms and the stability of the OH- ion in pyroxene using the infrared spectrum. They found four absorption bands for the OH- between ¶3350 and 3640 Cm-1 ie, frequencies below and above the frequency of isolate- ion at 3556 Cm-1. ¶ Lutz and his colleagues **[62-68] ¶Gennick and Harmon** **[69] Bates and al** **[70].** All show that the stretching frequency of the ion ¶ HO- is located in the red zone 3400-3700 ¶Cm-1. In aqueous solutions of KOH and NaOH, the IR and Raman spectra due to bound ions of -OHare found at 3610 Cm-1 **[61-73]**. ¶¶ he discussion was obscured for a long time by the fact that the fundamental frequency of the free -OH ion was experimentally and theoretically unavailable, and was suggested to study the high frequency of 3700 Cm-1 **[74]** of the metal cation **[47-77]** of and ¶ XH ….OH- hydrogen bonds **[63-69]** of the -OH ¶est ion corresponds to the new frequency compared in free -OH ion. ¶ Other reasons for the shifts in the bottom region have also been hypothesized, such as a partial covalence in the metal-oxygen bond, **[74]** and the existence of OH - ….X hydrogen bonds ¶ **[65]**.

¶ In 1982, based on evaluations of hydroxides with the non-H-bonded -OH ion, **¶Lutz, Echers, and Haeuseler [65]** predicted that the free -OH ion at a fundamental frequency that corresponds to 3570 ± 10 Cm-1 . They suggested that the metal- ion OH- causes upshifts of frequency wshifts. ¶XH….¶OH- and that the interaction is the main cause of downshift **[65].**

¶In 1983, Werner, Rosmus, and Reinsch **[78]** performed high level ab initio calculations and obtained a value of 3547 ¶Cm-1 for the main fundamental frequency l'-OH It was not known experimentally. principale fréquence fondamentale. ¶ Until 1985 was determined by Owrutsky et al the band of the -OH gas ¶3555.593 Cm-1 **[79].¶**

¶ n 1987 Lutz, Henning and Haeuseler **[66]** suggested that XH …..OH have the same properties as metal-oxygen, the repulsive part of the potential occurs in an upward passage of upshift frequency, consequently finding that the whilethe OH-….X hydrogen bonds are responsible for the frequency downshifts. ¶ Other molecular simulation work on the H+(H2O)n complex by two empirical models has been studied, nicknamed the hydronium model. The ¶H3O+ ion is considered as an elementary unit, with n-1 water molecules.. ¶ On the other hand, it is a reference of a proton model, the system is composed by simple molecules as follows: The proton is surrounded by water molecules with a number n. ¶ All four charges are considered in the polarizable model for the water molecule. Kozack and Jordan, **[80]** used the system to describe ion-water and water-water interactions; this work is consistent with experimental and quantum-mechanical studies **[81-85].** The hydronium ion and the proton represent two models, part of the interaction between the water molecule and the charged particle is determined by the electrostatic properties of the water model. ¶ The remaining part of the potential is para mastered to adjust such a description a proton in a water beam is realized. The two structural models are in good agreement with the ab initio calculations, the binding energies obtained in the proton model give an excellent result with the experiment **[86].**

¶ Recently the Lie group has developed the complement of two techniques to obtain the vibrational spectra of these hydrated ion beams. **[87-90].** he first approach is to attach a loosely bound M "messenger" molecule to the ion. ¶ The attached messenger is hoped to have only slight effect on the spectrumhe second approach is to obtain the IR spectra of such an ion by detecting its multi-photon dissociation, after exciting a vibrational transition (IRMPD). In this case, the spectrum obtained does not contain any disturbance by the messenger molecule.

Several theoretical studies concerning the structure, energy and frequencies of the ionic clusters of the hydronium ion **[91-102]** **H3O+**( **H2O** )**n=2,3,……9**, and the ionic aggregates of the hydroxide ion **[103-106]HO-**(**H2O**)**n=2,3…9,** show a great importance of these aggregates on the aqueous reactions in acid and base catalysis.

**I.5-** Hydration **M± (H2O) n :**

¶ n the recent works, they studied by theoretical calculations of simulations of the system

Cl-(H2O) n to determine the importance of quantum effects on structure and enthalpy [107]. They found, that there was a quantum delocalization of nuclei, particularly hydrogen, the calculated radial quantum distribution of functions are patterned and outwardly slightly less shifted compared to the corresponding classical description. ¶ Experimental studies of the solvation of I-(H2O)nin ion clusters have been performed by Kebarle and colleagues using high pressure mass spectrometry **[108].** By measuring the equilibrium constant of I- binder at different numbers of waters, they obtained the thermodynamic properties of iodide, which corresponds to the devan't Hoff equation. ¶ More recently, photoelectron spectroscopy has been employed by Markovich et al **[3,109** to study the solvation of I- (H2O)n where n varies from 1 to 60. From the binding energies of the beam, they were able to deduce the I-(H2O)n stabilization energies of the complex.

¶¶Theoretically, the solvation of iodide-water bundles has been studied by both electronic calculations classical molecular structure and simulation (dynamics). Combariza et al. By an SCF calculation with the MP2 method using the base 6-31+G \*¶ **[110]** hat their calculated stabilization energies agree with the experiment for beams with three or less water molecules. Recently, Dang and Garrett **[111]** studied by the photoelectron I-(H2O)n with n ranges from 1 to 15, using classical molecular simulations (dynamics). The simulated electron binding energies were disappointing with the work of Markovich et al.

The work done by David feller, Eric D. Glendening, Rick A. Kendall, and Kirk A. Peterson **[112]¶** on Li+(H2O)n, systems, n = 1 - by an ab initio Hartree-Fock calculation and the method from post-Hartree-Fock with an extensive basis, they determined the structures, bond energies, and enthalpies of small molecular beams. ¶.¶ The results were analyzed and compared with the experimental values, they determined that the Gaussian base perfection gives good coordination with the experimental values for the binding energy (20 kcal/mol or more) and the distance of Li+…O at a value of 0.1 Å By including the diffuse functions to take into account the lithium-water interaction, the latter gives a better modeling of the system, it can go up to 6 ligands which hydrate the lithium.¶ Thus the base of-p VDA gives results closer to the experimental values concerning the frequencies and the enthalpy of hydration **[112].**

¶ a study of the structural properties **[113]**of ¶Na+ (H2O)n), (n = 4,5,6,14) and Cl- (H2O)n with ¶(n = 4,5,6,7,8,14) clusters. They used two different potential models to describe the interactions of the molecules in the clusters. ¶ n one model (TIP4P) the potentials are in additive pairs, while in the second model (SPCE/POL) it takes into account many-body effects that are included explicitly, using polarization. ¶ The SPCE/POL model used in the calculations gives solvation enthalpy values which are in good agreement with the experimental values. ¶ The results also show that the cluster obtained in simulation with the SPCE/POL model are more energetically compared to the beams obtained by the simulations with the TIP4P model. ¶ The additional stability of these clusters is attributed to stronger water-ion interactions. For larger beams (n>6), the additional stability is also due to a reduction in water-water repulsion energy. ¶¶ They find that the structure of the cation in ther Na+(H2O)6 solvate cluster did not change when the two different potential models were employed. n 1991, the effect of polarizability and the sign of ionic charge were studied **[114]** in Cl-(H2O)20 clusters, using the molecular dynamics simulation technique.¶ They concluded that the reduction in ionic polarizability did not change significantly regarding the structure and dynamics of the Cl- (H2O)20 clusters, but the reversal of the sign of the ionic charge produced a large effect. ¶ The energetic considerations helped us to understand why Cl is located on the beam surface. By being on the surface the anion allows the creation of hydrogen. The bonded network between the water molecules and that lowers the total energy of the system. Simulations with the inverted sign of the ionic charge correspond to that of ¶"Cl+" ion which is similar in size and polarizability to a Cs+ ion **[115-116].**

In the same year other work [117] was carried out by Daniel Rose and Han Benjamin on the structural, energetic, and dynamic aspects of the solvation of Na+ and Cl- in water, the plantinum interface (100 ) is studied by molecular dynamic simulation. ¶¶¶¶¶ The mobility of ions near the interface is much less than that in the bulk, which also disagrees with models that do not take into account the existence of a strongly adsorbed layer in water.

II.6-Complexes :

olyatomic structures consist of a central ion or atom, surrounded by atoms, ions or molecules associated with the central atom by chemical bonds. Complexes are studied by coordination chemistry. Some complexes are made up of several central atoms: They are called polynuclear complexes, they form buildings called clusters when their metal atoms (central) are linked to each other.

Complexes can be neutral or charged, such as SO42- (ions (sulphate ion, complex of sulfur trioxide SO3 and O2-ion ) and Ag (NH3)2+. The entities linked to the central element, called ligands or ligands, can be ions made up of a single atom, such as halide ions (Cl-, Br-, etc.), neutral molecules, such as water (H2O) or ammonia (NH3), or ionic, organic or mineral molecules. The central ion is often a metal cation, as in Co (NH3)63+.

The bonds between the ligands and the central ion are coordination bonds, different from the classical chemical bonds (ionic, covalent, metallic, etc.). In general, ligands are electron donors (bases according to Lewis theory). They have at least one electron pair in their valence shell. The central ions or atoms are electron acceptors (acids in the Lewis sense). They have at least one free molecular orbital that can accept electron transfer from the ligands to the metal. We then obtain a much stronger bond than a classic bond: This is a coordination bond (or donor-acceptor of ligands). The complex is a ligand donor. The central ion is a ligand acceptor.

In solution, there is a chemical equilibrium between the complex, its ligands and the central ion in the free state. The reaction is as follows:

Acceptor + ligands ⇄ complex

That is : **A + *n*L ⇄ C**

With L the ligand, n the number of ligands per complex, C the complex (donor) and A the central ion (acceptor). Thus, for any complex, a ligand donor/acceptor pair can be defined, corresponding respectively to the complex/central ion pair.

From a quantum point of view, the coordination bonds between ligands and the central ion modify the electronic structure of the latter. Certain energy levels of the electrons are displaced, and the corresponding energy differences allow them to absorb radiation in the visible range. For this reason, solutions of transition metals are often very colorful. .

**I.7- Conclusion :**

The objective of this study is to present a certain number of the bibliographical study on the ionic complexes and to give a definition of the fundamental concepts on which one relies to approach our study concerning the neutral ionic complexes. On the other hand, the study consists in giving an outline on the interest of these complexes in the various fields.

The particular properties of the complexes come from the fact that the central ion (or atom) is protected from the influences of the external environment by the presence of ligands all around it. For example, when oxygen is complexed by hemoglobin, it can be transported without reacting with the various blood compounds. It will only be released at the level of the cells where, by attaching itself to their membranes, the hemoglobin will “open” to release the oxygen. Moreover, in the cavities protected by the ligands, particular reactions can occur which would be prevented by the ambient environment.

Many complexes are found in nature. For example, hemoglobin, which allows the transport of oxygen in the human body, is a complex made up of an iron atom linked to four donor nitrogen atoms that are part of a porphyric cycle, photosynthesis is ensured by a complex in chlorophyllous plants.

On the other hand, the chemical industry uses a large number of homogeneous catalysts, in particular those known as Ziegler-Natta, which are complexes. Mention may be made of the mixed organometallic complexes of titanium and aluminum which catalyze the polymerization of olefins and for which the chemists Ziegler and Natta obtained the Nobel Prize in Chemistry in 1963. The complexes are also used in chemical analysis to separate ions of a different nature, by liquid-liquid extraction.

**Chapter III. Quantum calculations on Hydration M± (H2O) n**

**III.1 Introduction :**

Solvation remains one of the most important questions in physics and chemistry. The mechanisms for energy transport and molecular motion provide important clues to the structure and dynamics of solvation and lead to progress towards a detailed understanding of the influence of the liquid environment on chemical reactions. The behavior of aqueous gas-phase beams can provide insight into the hydrogen bonding nature of these neutral ion complexes.

¶ The studies of the structure and the energy of the beams are very important in order to understand solvation phenomena in solution [1-3]. Experimentally, techniques such as mass spectrometry [1-3] and photoelectron spectrometry [4] are widely studied.

¶

he study of the properties of aqueous ionic solutions by an ab initio calculation on the systems (-OH)(H2O)n, with (n = 0..5), (H3O+)(H2O)n with (n = 0..5), (H+)(H2O)n with (n = 0..5) and (-OH,H3O+)(H2O)n with (n = 0, 1, 3), by three methods: Hatree-Fok , Moller Plesset Perturber , DFT with base 6-31+G\*\* which adapt to these different interactions and which include polarization effects.

The study of these systems allows us to examine the performance of the ab initio method used in solvation simulations. It also provides information on the structure, the number of hydration coordinates and the nature of the bonds of the neutral complexes.

**III.2** Calculation method **:**

Ab initio calculations [4] with different levels; Hartree-Fock (HF) self-coerent fields [5-16], the Moller-Plesset (MP) perturbation method [17], the density functional method (DFT) [18-22] these calculations were performed with the GAUSSIAN [23] with a Bernie[24] algorithm using the low 6-31+G\*\*[25] which includes polarization functions on all atoms. The influence of correlation energy has been determined by Moller-Plesset (MP) perturbation theory up to second order[26-27]. The MP methods were applied to the exclusion for the correction of the correlation energy calculations (approximate the frozen nucleus). Optimization at the MP2 level included all electrons in the correlation calculations. All geometric parameters have been completely optimized with the 6-31+G\*\* bass. Geometry optimizations were made with Schlegel's gradient optimization algorithm [28].

**III .3** Results and discussion**:**

**III.3.1.** Geometry**:**

**III.3.1.1.** System **(H3O+)(H2O)n with (n = 0..5) :**

**a. H3O+ :**

Geometry optimization by the HF method with the base 6-31+G\*\* of the hydroxide ion **H3O+** which has a C1 symmetry. The covalent bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom **H(2)** has an **O(1)-H(2)** distance of 0, 94308 Å. Another covalent bond formed by linking the oxygen atom **O(1)** the hydrogen atom **H(3)** has an **O(1)-H(3)** distance of 0, 943033 Å. The angle **H(2)-O(1)-H(3)** is 105.966538 deg, the **H(4)** atom lies out of plane with respect to the first with an angle of **H(4)-O(1)-H(3)** of 115.23856 deg . The  **O(1)-H(4)** distance is 0, 95419 Å.

To have more precision on the structure of this complex one makes an optimization of this geometry by two methods the method MP2 introduces the orbitals of correlation and the method DFT the results are gathered in Table III.1.

**Tables III. 1:** Geometric parameters calculated at different levels of the hydroxide ion and compared to experimental values.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Methods | | HF | MP2 | DFT |  |
| internal coordinate | |  |  |  | Data Experimental a |
| ψ(H(2)-O(1)-H(3)),°. | 105,96653 | | 105,966538 | 104, 33957 | 104,5 |
| ψ(H(4)-O(1)-H(3)),°. | | 115, 23856 | 115,23856 | 114, 39654 | 111,2 |
| R(O(1) -H(2)), [Å] | | 0, 94308 | 0, 94308 | 0, 964407 | 0, 950 |
| R(O(1) -H(3)), [Å] | | 0, 943033 | 0, 943033 | 0, 95985 | 0, 950 |
| R(O(1) -H(4)), [Å] | | 0, 95419 | 0, 95419 | 0, 968323 | 0, 950 |

aReference**[¶29]**

From the comparison of these results with the experimental values, it is deduced that the results found are in good agreement with the experimental values.

**b. H3O+(H2O) :**

Geometry optimization by the HF method with the 6-31+G\*\* base of the **H3O+ (H2O)** ion which has a C1 symmetry. The covalent bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom **H(2)** has an **O(1)-H(2)** distance of 0, 94342 Å. Another covalent bond formed by linking the oxygen atom **O(1)** to the hydrogen atom **H(3)** has an **O(1)-H(3)** distance of 0, 95014 Å. The angle **H(2)-O(1)-H(3)** is 107.966538 deg, the **H(4)** atom lies out of plane with respect to the first with an angle **H(4)-O(1)-H(3)** of 129.23856 deg the angle of **H(4)-O(1)-H(3)** of 91.23856 deg. The **O(1)-H(4)** distance 0, 95912 Å.

To have more precision on the structure of this complex one makes an optimization of this geometry by two methods the method MP2 introduces the orbitals of correlation and the method DFT the results are gathered in Table III. 2. Tables III. 2: Geometric parameters calculated at different levels of the H3O+ (H2O) ion and compared to experimental values.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Methods | | HF | MP2 | DFT |  |
| internal coordinate  ψ(H(2)-O(1)-H(3)),°. | | 107,96523 | 107,968438 | 107, 2657 | Data Experimental a  104,5 |
| ψ(H(2)-O(1)-H(3)),°. | 129, 71856 | | 129,8756 | 129, 3634 | 111,2 |
| ψ(H(2)-O(1)-H(3)),°. | | 91, 6124 | 91, 352 | 91, 659 | 104,5 |
| R(O(1) -H(2)), [Å] | | 0, 94548 | 0, 94365 | 0, 94879 | 0, 950 |
| R(O(1) -H(3)), [Å] | | 0, 9473 | 0, 94387 | 0, 95987 | 0, 950 |
| R(O(1) -H(4)), [Å]  R(O(1) ....H(5)), [Å] | | 0, 9519  2, 03102 | 0, 95462  2, 0298 | 0, 94235  2, 0265 | 0, 950  - |

aReference**[¶29]**

From the comparison of these results with the experimental values, it is deduced that the results found are in good agreement with the experimental values..

**c. H3O+(H2O)2 :**

Geometry optimization by the HF method with the 6-31+G\*\* base of the **H3O+ (H2O)2** ion which has a C1 symmetry. The covalent bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom **H(2)** has an **O(1)-H(2)** distance of 0, 94982 Å. nother covalent bond formed by linking the oxygen atom **O(1)** to the hydrogen atom **H(3)** has an **O(1)-H(3)** distance of 0, 95614 Å.

The angle **H(2)-O(1)-H(3)** is 107.60157 deg, the **H(4)** atom lies out of plane with respect to the first with an angle of **H(4)-O(1)-H(3)** of 129.70952 deg the angle of **H(4)-O(1)-H(3)** of 91.66754 deg. The  **O(1)-H(4)** distance is 0, 95854 Å.

To have more precision on the structure of this complex one makes an optimization of this geometry by two methods the method MP2 introduces the orbitals of correlation and the method DFT the results are gathered in Table III.3.

Tables III.3: Geometric parameters calculated at different levels of the **H3O+(H2O)2**  ion and compared to experimental values

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Methods | | HF | MP2 | DFT |  |
| internal coordinate  ψ(H(2)-O(1)-H(3)),°. | | 107,60157 | 107,968438 | 107, 2657 | Data Experimental a  104,5 |
| ψ(H(2)-O(1)-H(3)),°. | 129, 70952 | | 129, 8241 | 129, 5421 | 111,2 |
| ψ(H(2)-O(1)-H(3)),°. | | 91, 66754 | 91, 3564 | 91, 6548 | 104,5 |
| R(O(1) -H(2)), [Å] | | 0, 94548 | 0, 94365 | 0, 94879 | 0, 950 |
| R(O(1) -H(3)), [Å] | | 0, 9473 | 0, 94387 | 0, 95987 | 0, 950 |
| R(O(1) -H(4)), [Å]  R(O(1) ....H(5)), [Å]  R(O(1) ….H(6)), [Å]  R(O(1) ….H(7)), [Å] | | 0, 9519  2, 03102  2, 05943  2, 03196 | 0, 95462  2, 0298  2, 0721  2, 0312 | 0, 94235  2, 0265  2, 0645  2, 03145 | 0, 950  -  -  - |

aReference**[¶29]**

From the comparison of these results with the experimental values, it is deduced that the results found are in good agreement with the experimental values.

**d. H3O+(H2O)3 :**

Geometry optimization by the HF method with the 6-31+G\*\* base of the **H3O+ (H2O)3** on which has a C1 symmetry. The covalent bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom **H(2)** has an **O(1)-H(2)** distance of 0, 94329 Å. Another covalent bond formed by linking the oxygen atom **O(1)** to the hydrogen atom **H(3)** has an **O(1)-H(3)** distance of 0, 95031 Å.

The angle **H(2)-O(1)-H(3)** is 107.76208 deg, the **H(4)** atom lies out of plane with respect to the first with an angle of **H(4)-O(1)-H(3)** of 111.18067 deg the angle of **H(4)-O(1)-H(3)** of 117.47787 deg. The **O(1)-H(4)** distance is 0, 95062 Å.

To have more precision on the structure of this complex one makes an optimization of this geometry by two methods the method MP2 introduces the orbitals of correlation and the method DFT the results are gathered in Table III.4.

Tables III.4: Geometric parameters calculated at different levels of the **H3O+(H2O)2**  ion and compared to experimental values

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Methods | | HF | MP2 | DFT |  |
| internal coordinate  ψ(H(2)-O(1)-H(3)),°. | | 107,76208 | 106, 66836 | 107, 02972 | Data Experimental a  104,5 |
| ψ(H(2)-O(1)-H(3)),°. | 111, 18067 | | 117, 79395 | 115, 97013 | 111,2 |
| ψ(H(2)-O(1)-H(3)),°. | | 117, 47787 | 100, 52447 | 107, 02972 | 111,2 |
| R(O(1) -H(2)), [Å] | | 0, 94329 | 0, 96499 | 0, 96494 | 0, 950 |
| R(O(1) -H(3)), [Å] | | 0, 95062 | 0, 96491 | 0, 96493 | 0, 950 |
| R(O(1) -H(4)), [Å]  R(O(1) ....H(5)), [Å]  R(O(1) ….H(6)), [Å]  R(O(1) ….H(7)), [Å]  R(O(1) ….H(8)), [Å] | | 0, 95031  1, 98919  1, 93938  1, 99323  1, 99854 | 0, 97235  1, 89155  1, 812144  1, 9853  1.9854 | 0, 97983  1, 83348  1, 78738  1, 87911  1, 9658 | 0, 950  -  -  - |

aReference**[¶29]**

From the comparison of these results with the experimental values, it is deduced that the results found are in good agreement with the experimental values.

**f. H3O+(H2O)4 :**

Geometry optimization by the HF method with the 6-31+G\*\* base of the **H3O+ (H2O)4** ion which has a C1 symmetry. The covalent bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom **H(2)** has an **O(1)-H(2)** distance of 0, 95062 Å. Another covalent bond formed by linking the oxygen atom **O(1)** to the hydrogen atom **H(3)** has an **O(1)-H(3)** distance of 0, 95068 Å.

The angle **H(2)-O(1)-H(3)** is 108.34776 deg, The **H(4)** atom lies out of plane with respect to the first with an angle of **H(4)-O(1)-H(3)** of 152.48449 deg, The angle of **H(4)-O(1)-H(3)** of 90.39249 deg. The **O(1)-H(4)** distance is 0, 9654 Å.

To have more precision on the structure of this complex one makes an optimization of this geometry by two methods the method MP2 introduces the orbitals of correlation and the method DFT the results are gathered in Table III.5.

Tables III. 5: The geometric parameters calculated at different levels of the **H3O+(H2O)4**  ion and compared to the experimental values.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Methods | | HF | MP2 | DFT |  |
| internal coordinate  ψ(H(2)-O(1)-H(3)),°. | | 108, 34776 | 108, 76836 | 108, 02522 | Data Experimental a  104,5 |
| ψ(H(2)-O(1)-H(3)),°. | 152, 48449 | | 152, 75395 | 152, 87213 | 111,2 |
| ψ(H(2)-O(1)-H(3)),°. | | 90, 39249 | 90, 53847 | 90, 41272 | 111,2 |
| R(O(1) -H(2)), [Å] | | 0, 95062 | 0, 95021 | 0, 9562 | 0, 950 |
| R(O(1) -H(3)), [Å] | | 0, 95068 | 0, 96241 | 0, 95124 | 0, 950 |
| R(O(1) -H(4)), [Å]  R(O(1) ....H(5)), [Å]  R(O(1) ….H(6)), [Å]  R(O(1) ….H(7)), [Å]  R(O(1) ….H(8)), [Å]  R(O(1) ….H(9)), [Å] | | 0, 95067  1, 9721  1, 97838  1, 99853  1, 99854  1, 9865 | 0, 95124  1, 9723  1, 812144  1, 9853  1.9854  1, 9851 | 0, 95213  1, 96348  1, 78738  1, 87911  1, 9658  1, 95648 | 0, 950  -  -  -  -  - |

aReference**[¶29]**

From the comparison of these results with the experimental values, it is deduced that the results found are in good agreement with the experimental values.

**III 3..1.2.** System **(H+)(H2O)n with (n = 1..5)**

**a. H+(H2O) :**

Geometry optimization by the HF method with the 6-31+G\*\* base of the **H+ (H2O)** to the hydrogen atom ion which has aC1 symmetry. The hydrogen bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom **H(2)** has an **O(1)…H(2)** distance of 4, 16909 Å.

To have more precision on the structure of this complex one makes an optimization of this geometry by two methods the method MP2 introduces the orbitals of correlation and the method DFT the results are gathered in Table III.6

Tables III.6: Geometric parameters calculated at different levels of the **H3O+(H2O)**  ion and compared to experimental values .

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Methods | | HF | MP2 | DFT |  |
| internal coordinate  ψ(H(2)-O(1)-H(3)),°. | | 84, 44768 | 139, 0511 | 59, 70603 | Data Experimental a  104,5 |
| ψ(H(2)-O(1)-H(3)),°. | 138, 7411 | | 84, 64474 | 136, 13374 | 111,2 |
| ψ(H(2)-O(1)-H(3)),°. | | 107, 4723 | 105, 4223 | 106, 48267 | 104,5 |
| R(O(1) -H(2)), [Å] | | 0, 94306 | 0, 96317 | 0, 96611 | 0, 950 |
| R(O(1) -H(3)), [Å] | | 0, 94307 | 0, 96318 | 0, 96522 | 0, 950 |
| R(O(1) ....H(4)), [Å] | | 4, 16909 | 4, 01703 | 3, 48163 | - |

aReference**[¶29]**

From the comparison of these results with the experimental values, it is deduced that the results found are in good agreement with the experimental values.

**b. H+(H2O)2 :**

Geometry optimization by the HF method with the 6-31+G\*\* base of the **H+ (H2O)2** ion which has a C1 symmetry.

To have more precision on the structure of this complex one makes an optimization of this geometry by two methods the method MP2 introduces the orbitals of correlation and the method DFT the results are gathered in Table III.7.

Tables III.7: Geometric parameters calculated at different levels of the **H3O+(H2O)2** ion and compared to experimental values..

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Methods | | HF | MP2 | DFT |  |
| internal coordinate  ψ(H(2)-O(1)-H(3)),°. | | 33, 36727 | 83, 88408 | 35, 94828 | Data Experimental a  104,5 |
| ψ(H(2)-O(1)-H(3)),°. | 133, 21095 | | 137, 19495 | 135, 5120 | 111,2 |
| ψ(H(2)-O(1)-H(3)),°. | | 106, 86044 | 107, 87124 | 109, 7137 | 104,5 |
| R(O(1) -H(2)), [Å] | | 0, 9321 | 0, 95050 | 0, 96126 | 0, 950 |
| R(O(1) -H(3)), [Å] | | 0, 94344 | 0, 94254 | 0, 95618 | 0, 950 |
| R(O(1) ....H(4)), [Å]  R(O(1) ….H(5)), [Å] | | 3, 65899  3, 67600 | 2, 89177  2, 88022 | 2, 90908  2, 63223 | -  - |

aReference**[¶29]**

From the comparison of these results with the experimental values, it is deduced that the results found are in good agreement with the experimental values.

**c. H+(H2O)3 :**

Geometry optimization by the HF method with the 6-31+G\*\* base of the **H+ (H2O)3** ion which has a C1 symmetry.

To have more precision on the structure of this complex one makes an optimization of this geometry by two methods the method MP2 introduces the orbitals of correlation and the method DFT the results are gathered in Table III.8.

Tables III.8: Geometric parameters calculated at different levels of the **H3O+(H2O)2**  ion and compared to experimental values.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Methods | | HF | MP2 | DFT |  |
| internal coordinate  ψ(H(2)-O(1)-H(3)),°. | | 123, 5242 | 127, 15361 | 121, 05694 | Data Experimental a  104,5 |
| ψ(H(2)-O(1)-H(3)),°. | 118, 23067 | | 119, 4107 | 130, 64614 | 111,2 |
| ψ(H(2)-O(1)-H(3)),°. | | 107, 46287 | 106, 7987 | 106, 71112 | 111,2 |
| R(O(1) -H(2)), [Å] | | 0, 96567 | 0, 96265 | 0, 98094 | 0, 950 |
| R(O(1) -H(3)), [Å] | | 0, 93455 | 0, 97512 | 0, 96690 | 0, 950 |
| R(O(1) ...H(4)), [Å]  R(O(1) ....H(5)), [Å]  R(O(1) ….H(6)), [Å]  R(O(1) ….H(7)), [Å]  R(O(1) ….H(8)), [Å]  R(O(1) ….H(9)), [Å]  R(O(1) ….H(10)), [Å] | | 2, 97191  4, 61106  4, 07619  3, 99854  1,96541  1, 98624 | 3, 99364  4, 42496  4, 83602  1, 91446  1.94501  1, 92045 | 2, 31545  2, 95776  4, 12632  1, 81053  1, 87733  2, 71822 | 0, 950  -  -  -  -  - |

aReference**[¶29]**

From the comparison of these results with the experimental values, it is deduced that the results found are in good agreement with the experimental values.

**d. H+(H2O)4 :**

Geometry optimization by the HF method with the 6-31+G\*\* base of the **H+ (H2O)4** ion which has a C1 symmetry.

To have more precision on the structure of this complex one makes an optimization of this geometry by two methods the method MP2 introduces the orbitals of correlation and the method DFT the results are gathered in Table III.9

Tables III.9: Geometric parameters calculated at different levels of the **H3O+(H2O)4** ion and compared to experimental values.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Methods | | HF | MP2 | DFT |  |
| internal coordinate  ψ(H(2)-O(1)-H(3)),°. | | 75, 02795 | 77, 00803 | 71, 48848 | Data Experimental a  104,5 |
| ψ(H(2)-O(1)-H(3)),°. | 148, 84141 | | 167, 11768 | 68, 994632 | 111,2 |
| ψ(H(2)-O(1)-H(3)),°. | | 107, 29644 | 106, 32678 | 106, 79023 | 111,2 |
| R(O(1) -H(2)), [Å] | | 0, 95304 | 0, 98031 | 0, 98604 | 0, 950 |
| R(O(1) -H(3)), [Å] | | 0, 94281 | 0, 96915 | 0, 96442 | 0, 950 |
| R(O(1) ....H(4)), [Å]  R(O(1) ....H(4)), [Å]  R(O(1) ….H(4)), [Å]  R(O(1) ….H(4)), [Å]  R(O(1) ….H(4)), [Å]  R(O(1) ….H(4)), [Å]  R(O(1) ….H(4)), [Å]  R(O(1) ….H(4)), [Å]  R(O(1) ….H(4)), [Å] | | 4, 07572  3, 80879  3, 91300  4, 98315  1, 94721  1, 93430  1, 94479  1, 94311 | 3, 96894  3, 77855  3, 89568  4, 03613  1, 81852  1, 79725  1, 81774  1, 79666 | 3, 37517  3, 55753  3, 51201  3, 46975  1, 76754  1, 76552  1, 75799  1, 75073 | 0, 950  -  -  -  -  -  -  - |

aReference**[¶29]**

From the comparison of these results with the experimental values, it is deduced that the results found are in good agreement with the experimental values.

**III 3.1.3.** System **(-OH)(H2O)n, with (n = 0..5)**

**a. HO- :**

Geometry optimization by the HF method with the base 6-31+G\*\* of the hydronym ion **HO-** which has a Cv symmetry. The covalent bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom  **H(2)** has an **O(1)-H(2)** distance of 0, 95504 Å.

To have more precision on the structure of this complex one made an optimization of this geometry by two methods the method MP2 by introducing the orbitals of correlation and the method DFT, the results are mentioned in Table III.10.

Tables III.10: Geometric parameters calculated at different levels of the hydronym ion and compared to experimental values.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Methods | HF | MP2 | DFT |  |
| internal coordinate |  |  |  | Data Experimental a |
| R(O(1) -H(2)), [Å] | 0, 95504 | 0, 97323 | 0, 955041 | 0, 964 |

aReference **[¶30] 55**

From the comparison of these results with the experimental values it is deduced that the results found are in good agreement with the experimental results.

**b. HO-(H2O) :**

Geometry optimization by the HF method with the base 6-31+G\*\* of the **HO-(H2O)** on which has Cv symmetry, the ion stabilizes at an energy level of -0.120135 K Cal/Mol

The covalent bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom **H(2)** has an **O(1)-H(2)** distance of 0, 96030 Å.

To have more precision on the structure of this complex one made an optimization of this geometry by two methods the method MP2 by introducing the orbitals of correlation and the method DFT, the results are mentioned in Table III.11.

Tables III.11: Geometric parameters calculated at different levels of the **HO-(H2O) ion** and compared to experimental values..

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Methods | HF | MP2 | DFT |  |
| internal coordinate |  |  |  | Data Experimental a |
| R(O(1) -H(2)), [Å]  R(O(1) ..H(3)), [Å] | 0, 96030  1, 96816 | 0, 97533  1, 99654 | 0, 98072  1, 98541 | 0, 964  - |

aReference**[¶30]**

From the comparison of these results with the experimental values it is deduced that the results found are in good agreement with the experimental results

**c. HO-(H2O)2 :**

Geometry optimization by the HF method with the base 6-31+G\*\* of the ion **HO-(H2O)2** which has a Cv symmetry. he covalent bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom  **H(2)** has an  **O(1)-H(2)** distance of 0, 96226 Å.

To have more precision on the structure of this complex one made an optimization of this geometry by two methods the method MP2 by introducing the orbitals of correlation and the method DFT, the results are mentioned in Table III.12**.**

Tables III.12: Geometric parameters of **HO-(H2O)2**  ion calculated at different system levels and compared to experimental values.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Methods | HF | MP2 | DFT |  |
| internal coordinate |  |  |  | Data Experimental a |
| R(O(1) -H(2)), [Å]  R(O(1) ..H(3)), [Å] R(O(1) ..H(4)), [Å]  R(O(1) ..H(5)), [Å] | 0, 9226  1, 97356  2, 04505  2, 24783 | 0, 98522  1, 88108  1, 93742  2, 12254 | 0, 996521  1, 81682  2, 04336  1, 8907 | 0, 964  -  -  - |

aReference **[¶30]**

From the comparison of these results with the experimental values it is deduced that the results found are in good agreement with the experimental results.

**d. HO-(H2O)3 :**

Geometry optimization by the HF method with the base 6-31+G\*\* of the ion **HO-(H2O)3** which has aCv symmetry. The covalent bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom **H(2)** has an **O(1)-H(2)** distance of 0, 96515 Å.

To have more precision on the structure of this complex one made an optimization of this geometry by two methods the method MP2 by introducing the orbitals of correlation and the method DFT, the results are mentioned in Table III.13.

Tables III.13: Geometric parameters calculated at different system levels and compared to experimental values.

**Tableaux III.13:** Les paramètres géométriques calculés à différents niveaux de système et comparés aux valeurs expérimentales.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Methods | HF | MP2 | DFT |  |
| internal coordinate |  |  |  | Data Experimental a |
| R(O(1) -H(2)), [Å]  R(O(1) ..H(3)), [Å]  R(O(1) ..H(6)), [Å]  R(O(1) ..H(4)), [Å]  R(O(1) ..H(5)), [Å] | 0, 96515  1, 89704  2, 05506  2, 36523  2, 14539 | 0, 96875  1, 88954  2, 03742  2, 4215  2, 1548 | 0, 98754  1, 89854  2, 05124  2, 0248  2, 15487 | 0, 964  -  -  -  - |

aReference **[¶30]**

From the comparison of these results with the experimental values it is deduced that the results found are in good agreement with the experimental results.

**e. HO-(H2O)4 :**

Geometry optimization by the HF method with the base 6-31+G\*\* of the ion **HO-(H2O)4** which has a Cv symmetry. he covalent bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom **H(2)** has an **O(1)-H(2)** distance of 0, 97197 Å.

To have more precision on the structure of this complex one made an optimization of this geometry by two methods the method MP2 by introducing the orbitals of correlation and the method DFT, the results are mentioned in Table III.14.

Tables III.14: Geometric parameters calculated at different system levels and compared to experimental values.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Methods | HF | MP2 | DFT |  |
| internal coordinate |  |  |  | Data Experimental a |
| R(O(1) -H(2)), [Å]  R(O(1) ..H(3)), [Å]  R(O(1) ..H(4)), [Å]  R(O(1) ..H(5)), [Å]  R(O(1) ..H(6)), [Å]  R(O(1) ..H(7)), [Å]  R(O(1) ..H(8)), [Å] | 0, 97197  1, 79228  2, 54130  2, 19735  1, 99395  1, 97280  2, 10887 | 0, 98421  1, 54108  1, 69742  2, 12314  1, 98741  2, 2164  2, 02135 | 0, 98341  2, 06977  1, 82595  1, 97490  2, 46418  1, 93313  1, 97490 | 0, 964  -  -  -  -  -  - |

aReference **[¶30]**

From the comparison of these results with the experimental values it is deduced that the results found are in good agreement with the experimental results.

**III3..1.4.** System **(-OH,H3O+)(H2O)n with (n = 0, 1, 3)**

**a.** Neutral complex **(-OH, H3O+):**

Geometry optimization of the neutral complex **(-OH, H3O+)** stabilizes the system, the acceptor monomer has three covalent bonds, where two of them are in the plane (**O(1)-O(5)-H(6)**). The covalent bond formed by the bond of the oxygen atom **O(1)** to the hydrogen atom  **H(4)** has an **O(1)-H(4)** distance of 0, 989127 Å.

The **H(3)-O(1)-H(4)** angle is 112, 841 deg, the **H(2)** atom lies out of plane, the an angle of **H(3)-O(1)-H(2)** is 109, 548 deg . **O(1)-H(2)** distance is 0, 95419 Å, angle is **H(2)-O(1)-H(4)** These three angles are close to 107, 891 deg, These three angles are close to 120 deg, he formation of the **H3O+** ion is planar. The donor monomer has two bonds, one has characteristics of an **R O(5)…H(4),** hydrogen bond, the distance is 2, 001234 Å. The angle **O(5)-H(4)-O(1)** is 150, 594 deg, This angle of 150, 594 deg is close to 180 deg, the hydrogen **H(4)** is on a linear bond , confirming that the system maintains its **C1** symmetry and the other by an **O(5)-H(6)** covalent bond at a distance of 0, 93984 Å. The angle of **H(4)-O(5)-H(6)** is 106, 394 deg.

To have more precision on the structure of this complex one made an optimization of this geometry by two methods the method MP2 by introducing the orbitals of correlation and the method DFT, the results are in Table III.15.

Tables III.15: Geometric parameters calculated at different levels of the system **(-OH, H3O+)** and compared to experimental values.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Methods / internal coordinate | HF | MP2 | DFT | Data Experimental a |
| R(O(1) -H(4)), [Å] | 0, 945419 | 0, 964229 | 0, 965862 | 0, 950 |
| R(O(1) -H(3)), [Å] | 0,96353 | 0, 97561 | 0, 965859 | 0, 950 |
| ψ(H(3)-O(1)-H(2)),°. | 107, 891 | 109, 748 | 104, 33957 | 104.5 |
| ψ(H(3)-O(1)-H(4),°. | 112, 841 | 113, 1234 | 114, 39654 | 111, 2 |
| R(O(5) -H(6)), [Å] | 0, 93984 | 0, 94674 | 0, 964033 | 0, 950 |
| R(O(5) -H(4)), [Å] | 2, 001234 | 2, 009184 | 1, 923828 | - |

aReference **[¶29]**

A comparison of the results found with the experimental values shows that the HF method is close to the experimental of 0.04008% compared to the DFT method of 0.04358% and the MP2 method of 0.04226%.

**b.** Neutral complex **(-OH, H3O+)( H2O):**

Geometry optimization of the neutral complex **(-OH, H3O+)( H2O)** stabilizes the system, the acceptor monomer has three covalent bonds, where two of them are in the plane (**O(1)-O(2)-O(3)**). **(-OH, H3O+)( H2O)** stabilizes the system, the acceptor monomer has three covalent bonds, where two of them are in the (**O(1)-O(2)-O(3)**). The new covalent bond formed by linking the oxygen atom **O(2)** to the hydrogen atom **H(5)** has an  **O(2)-H(5)** distance of 0, 978915 Å. The **O(2)-H(7)** distance is 0, 969815 Å. The angle **H(7)-O(2)-H(5)** is 111, 815 deg,. Angle **O(1)-H(5)-O(2)** is 152, 016 deg, the other  **H(4)** lies outside the plane ( **O(3)-O(1)-O(2)** ), it forms with **H(7)** an angle **H(7)-O(2)-H(4)** of 109, 454 deg. The **O(2)-H(4** distance is0, 95815 Å, the **H(5)-O(2)-H(4)** angle is 109, 508 deg. These three angles are close to120 deg, the formation of the **H3O+** ion is planar.The donor monomer has two bonds, one has characteristics of an **O(1)…H(5),** hydrogen bond, the distance is 2, 078153 Å, The angle **O(1)-H(5)-O(2)** is 152, 016 deg. This angle of 152, 016 deg is close to 180 deg, the hydrogen **H(5)** is on a linear bond, which confirms that the system retains its C1 symmetry and the other by a covalent bond **C1** symmetry and the other by a covalent bond **O(1)-H(8)** at a distance of 0, 93984 Å. The angle of **H(5)-O(1)-H(8)**  is 112, 020 deg. **H(7)**  is bonded to **O(3)** by a hydrogen bond at an **O(3)…H(7)** distance of 1, 60323 Å by HF. The oxygen atom **O(3)** participates in two covalent bonds one **O(3)-H(9)** is in the plane(**O(1)-O(2)-O(3)**) at a distance of 0, 99346 Å by HF. the other **O(3)-H(6)** bond is above the plane has a distance of 0, 94252 Å by HF and by a hydrogen bond where the **H(9)**  is bonded to **O(1)** at a distance **O(1)…H(9)** of 1,62292 Å by HF, The angle **H(5)-O(1)-H(8)** is 112, 020 deg by HF. The **H(5)-O(2)-H(7)** angle is 111, 815 deg by HF, The **H(5)-O(2)-H(4)** angle is 109, 508 deg by HF. The **H(7)-O(2)-H(4)** angle is 109, 454 deg by HF. The **O(2)-H(7)-O(3)** angle is 153, 489 deg by HF. The **H(7)-O(3)-H(9)** angle is 87, 938 deg by HF, The **H(7)-O(3)-H(6)** angle is 114, 687 deg by HF. The **H(6)-O(3)-H(9)** angle is 108, 63 deg . The **O(3)-H(9)-O(1)** angle is 155, 119 deg by HF,. The **H(9)-O(1)-H(5)** angle is 81, 191 deg by HF. The **H(9)-O(1)-H(8)** angle is 112, 149 deg by HF.

To have more precision on the structure of this complex one makes an optimization of this geometry by two methods the MP2 method introduces the orbitals of correlation and the DFT method, the results are mentioned in Table III.16.

Tables III.16: Geometric parameters calculated at different levels of the system **(-OH, H3O+)(H2O)**  and compared to experimental values.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Methods / internal coordinate | HF | MP2 | DFT | Data Experimental a |
| R(O(2) –H(5)), [Å] | 0, 978915 | 0, 987315 | 0, 980092 | 0, 950 |
| R(O(2) –H(4)), [Å] | 0,95815 | 0, 96660 | 0, 964338 | 0, 950 |
| ψ(H(7)-O(2)-H(4)),°. | 109, 452 | 109, 658 | 110,0256 | 104.5 |
| ψ(H(7)-O(2)-H(5),°. | 111, 815 | 111, 991 | 117, 8444 | 111, 2 |
| R(O(1) –H(8)), [Å] | 0, 93984 | 0, 91478 | 0, 964033 | 0, 950 |
| R(O(1) –H(5)), [Å] | 1, 92891 | 1, 821697 | 1, 791924 | - |

aReference **[¶29]**

A comparison of the results found with the experimental values shows that the HF method is close to the experimental of 0.04008% compared to the DFT method of 0.04358% and the MP2 method of 0.04226%.

**c.** Neutral complex **(-OH, H3O+)(H2O)3:**

Geometry optimization of the neutral complex **(-OH, H3O+)(H2O)3** stabilizes the system, the acceptor monomer has three covalent bonds, where two of them are in the plane (**O(1)-O(6)-O(9)**). The new covalent bond formed by the bond of the oxygen atom **O(6)** to the hydrogen atom **H(2)** has an **O(2)-H(6)** distance of 0, 97123 Å and the **O(6)-H(13)** is 0, 97342 Å. The angle **H(13)-O(6)-H(2)** is 113, 849 deg. The other  **H(8)** lies out of plane by an angle of **H(13)-O(6)-H(8)** of 105, 637 deg.The  **O(6)-H(8)** distance is 0, 959813 Å.

The angle **H(8)-O(6)-H(2)** is 109, 840 deg. These three angles are close to 120 deg, the formation of the **H3O+** ion is planar.Le détenteur possède deux liaisons, l'une à des caractéristiques d'une liaison hydrogène **O(1)…H(2),** la distance est de2, 099134 Å. The **O(1)-H(2)-O(6)** angle is158, 087 deg. This angle of 158, 087 deg is close to 180 deg, the **H(4)** is on a linear bond, which confirms that the system retains its Cs symmetry and the other by a covalent **Cs** et l'autre par une liaison covalente **O(1)-H(3)** at a distance of 0, 932013 Å. The angle of **H(2)-O(1)-H(3)**  is 108, 091 deg. The oxygen atom **O(1)** has two hydrogen bonds one has an **O(1)…H(4)** distance of 1, 60132 Å by HF and the other **O(1)….H(5)** distance ) of 1, 73768 Å by HF. The **O(6)-H(8)** bond is out of plane (**O(1)-O(9)-O(6)**) has a distance of 0, 959813 Å by HF. The oxygen atom **O(9)** participates in two covalent bonds **O(9)-H(4)** is in the plane (**O(1)-O(9)-O(6)**) at a distance of 0, 98561 Å by HF, the other **O(9)-H(10)** bond is out of plane has a distance of 0, 94353 Å by HF and by a hydrogen bond where the **H(13)**  is bonded to **O(9)** at an **O(9)…H(13)** distance of 1, 60213 Å by HF. The **O(6)-H(13)-O(9)** angle is 147, 399 deg par HF. L'angle **H(13)-O(9)-H(4)** est de 88, 390 deg par HF. L'angle **H(13)-O(9)-H(10)** est de 114, 642 deg by HF. The **H(4)-O(9)-H(10)** angle is 121, 169 deg by HF. The **O(9)-H(4)-O(1)** angle is 149, 085 deg by HF. The **H(4)-O(1)-H(2)** angle is 81, 327 deg by HF. The **H(4)-O(1)-H(3)** angle is 122, 362 deg by HF.

To have more precision on the structure of this complex one makes an optimization of this geometry by two methods the method MP2 introduces the orbitals of correlation and the method DFT the results are mentioned in Table III.17.

Tables III.17: Geometric parameters calculated at different levels of the system **(-OH, H3O+)(H2O)3**  and compared to experimental values.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Methods / internal coordinate | HF | MP2 | DFT | Data Experimental a |
| R(O(6) –H(2)), [Å] | 0, 97123 | 0, 98345 | 0, 979645 | 1, 017± 0.005a  1, 01± 0.01b |
| R(O(6) –H(8)), [Å] | 0,959813 | 0, 959912 | 0, 964084 | 1, 017±0.005a  1, 01±0.01b |
| ψ(H(13)-O(6)-H(8)),°. | 105, 637 | 107, 158 | 108, 15347 | 104.5 c |
| ψ(H(13)-O(6-H(2)),°. | 111, 815 | 113, 963 | 118, 15347 | 111,2 c |
| R(O(1) –H(3)), [Å] | 0, 932013 | 0, 93526 | 0, 980007 | 1, 017±0.005a  1, 01±0.01b |
| R(O(2) –H(1)), [Å] | 2, 099134 | 2, 03678 | 2, 040007 | - |

aReference **[¶31]** , bReference **[¶32],** cReference **[¶29]**

The comparison of the results found with the experimental values shows that the DFT method is close to the experimental of 0.0152% compared to the HF method of 0.0215% and the MP2 method of 0.0243%.

**III.3.2.** Frequency**:**

**III.3.2.1.** System **(H3O+)(H2O)n with (n = 0..5) :**

**a. H3O+ :**

The optimization of an H3O ion by the different levels by the final structure, the frequency represented in Table III.18 was calculated.

Table III.18: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the H3O+ structure with C3v symmetries.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  O-H Stretch  H-O-H Torsion  H-O-H Bend  H-O-H Torsion  H-O-H Torsion | 3970, 31  3821, 02  1641, 52  472, 88  257, 651  186, 08 | 57, 4022  9, 5738  95, 3635  0, 5101  162, 222  94, 9409 | 4264, 65  4147, 67  1769, 59  79, 29  39, 557  30, 7989 | 58, 1494  16, 3398  104, 376  2, 808  310, 971  12, 1201 | 3912, 07  3789, 49  1617, 56  416, 101  160, 487  53, 2028 | 46, 7261  4, 6474  93, 1174  0, 5219  158, 234  96, 267 |

We note the appearance of two bands in the interval from 3700 to 4300 Cm-1 with high intensities, which correspond to the O-H Stretch (an unbound free valence frequency). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1 [33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**b. H3O+(H2O):**

The optimization of an **H3O+(H2O** by the different levels by the final structure, we have calculated the frequency represented in Table III.19.

Table III.19: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of H3O+**(H2O)** structure with C3v symmetries.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  O-H Stretch  H..(H-O-H) Out of plane donor bend | 3990, 31  3861, 02  501 ,1  591,8 | 554, 4022  41, 5738  21,12  52,1 | 4664, 65  4657, 67  611,9  663,2 | 585, 1494  206, 3398  21,36  54,89 | 3962, 07  3799, 49  632,35  661,9 | 56, 7261  32, 6474  12,5  153,8 |

We note the appearance of two bands in the interval from 3700 to 4300 Cm-1 with high intensities, which correspond to the O-H Stretch (an unbound free valence frequency). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1[33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**c. H3O+(H2O)2 :**

The optimization of an **H3O+(H2O)2** ion by the different levels by the final structure, we have calculated the frequency represented in Table III.20.

Table III.20: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the H3O+**(H2O)** structure with a C3v symmetry

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  H..(H-O-H) Out of plane donor bend | 3990, 31  3861, 02  3954,21  3451,2  3521,6  3854,22  501 ,1  591,8 | 554, 4022  46, 5738  91,12  22,1  29,2  35,25  58,24  14,52 | 4032, 94  4064, 98  4069, 95  4237, 18  4241, 02  4242, 6  611,9  663,2 | 8, 9655  325, 849  291, 387  151, 156  142, 107  144, 125  36,24  651,28 | 3952, 07  3759, 49  3981,75  3951,38  3954,25  2645,98  632,35  661,9 | 598, 7261  325 6474  82,5  141,8  25,14  35,82  321,95  854,72 |

We note the appearance of two bands in the interval from 3700 to 4300 Cm-1 with high intensities, which correspond to the O-H Stretch (a frequency of unbound free valence). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1[33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**d. H3O+(H2O)3 :**

The optimization of an**H3O+(H2O)3** ion by the different levels by the final structure, the frequency represented in Table III.21 was calculated.**.**

Table III.21: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the H3O+**(H2O)3** structure with a C3v symmetry.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  H..(H-O-H) Out of plane donor bend | 3571,36  3746,89  3781,17  3890,75  3885,79  3945,94  3984,37  3989,08  743,88  641,78  471,12 | 554, 4022  46, 5738  91,12  22,1  29,2  35,25  58,24  14,52  158,757  252,814  19,8753 | 4012,09  4063, 82  4067,64  4138,57  4221,57  4230, 52  4239, 45  4256, 88  799, 05  701,823  627,475 | 548, 923  155, 759  204,21  36, 3059  134, 286  165,495  124,102  131, 838  321,424  213,511  181,246 | 3425,5  3589,24  3636,55  3718,9  3875,7  3887,4  3890,63  3891,48  797,023  699,523  461,087 | 806, 346  490,439  444,696  124,958  84,7843  104,347  159,97  25,9637  99,1849  315,313  122,695 |

We note the appearance of two bands in the interval from 3700 to 4300 Cm-1 with high intensities, which correspond to the O-H Stretch (a frequency of unbound free valence). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1[33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**e. H3O+(H2O)4 :**

The optimization of an**H3O+(H2O)4** ion by the different levels by the final structure, we have calculated the frequency represented in Table III.22.

Table III.22: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the H3O+**(H2O)** structure with a C3v symmetry.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  H..(H-O-H) Out of plane donor bend | 3987,4  3524,51  3924,1  2812,5  3254,3  3624,2  3725,4  3541,6  3841,2  3951,8  754,25  628,3  698,2 | 548,65  524,12  958,24  58,124  752,.32  741,3  254,69  245,69  254,1  248,3  249,24  417,2  451,08 | 4011,35  4036,91  4058,68  4063,17  4068,84  4128,56  4237,54  4239,99  4240,44  4240,85  799, 05  701,823  627,475 | 44,3655  190,164  165,431  451,291  143,72  516,271  187,03  207,445  105,404  85,4637  103,842  4,4964  520,715 | 3396,21  3488,55  3503,44  3544,49  3812,27  3917,45  3920,56  3932,38  3952,24  3658,28  716,457  679,058  643,569 | 81,6559  1390,7  1306,63  206,17  108,599  90,3798  78,9348  101,125  25,85  654,87  62,101  66,993  200,21 |

We note the appearance of one of the bands in the interval from 3700 to 4300 Cm-1with high intensities, which correspond to the O-H Stretch (an unbound free valence frequency). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1 [33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**III.3.2.2.** System **(H+)(H2O)n with (n = 1..5)**

**a. H+(H2O):**

Optimization of an **H+(H2O)** by the different levels by the final structure, the frequency represented in Table III.23 was calculated.

Table III.23: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the H+**(H2O)**  structure with C3v symmetry

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  O-H Stretch  H..(H-O-H) Out of plane donor bend | 3866,92  4013,8 | 10,0752  66,486 | 4149,22  4271,43 | 24,987  92,3902 | 3797,97  3926,61 | 6,4518  59,4301 |

We note the appearance of one of the bands in the interval from 3700 to 4300 Cm-1 with high intensities, which correspond to the O-H Stretch (an unbound free valence frequency). These bands are in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1 [33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**b. H+(H2O)2 :**

The optimization of an **H+(H2O)2** ion by the different levels by the final structure, the frequency represented in Table III.24 was calculated.

Table III.24: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the H+**(H2O)2** structure with a C3v symmetry

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  H..(H-O-H) Out of plane donor bend | 3857, 98  3862, 42  4004, 81  4008, 22 | 10, 877  10, 721  74, 108  67, 126 | 4146, 92  4151, 95  4266, 65  4273, 63 | 22, 429  23, 073  97, 085  92, 593 | 3862, 92  3901, 26  4031, 99  4035, 21 | 25, 383  11,220  66, 041  87, 034 |

We note the appearance of two bands in the interval from 3700 to 4300 Cm-1 with high intensities, which correspond to the O-H Stretch (a frequency of unbound free valence). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1[33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**c. H+(H2O)3 :**

The optimization of an **H+(H2O)3** ion by the different levels by the final structure, the frequency represented in Table III.25 has been calculated.

Table III.25: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the H+**(H2O)3** structure with a C3v symmetry

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  H..(H-O-H) Out of plane donor bend | 3983,17  3259,76  3967,47  3945,7  3882,06  3126,22  895,056  783,297  493,372 | 84,1  54,2  54,3  69,4  85,2  64,78  85,1  75,4  987,2 | 3881,66  4072,43  4117  4225, 57  4275,02  4344,93  684, 956  631,525  468,76 | 93,0625  188,3  46,0944  247,168  151,995  79,2855  245,664  84,7686  53,5463 | 3533,17  3589,76  3717,47  3855,7  3865,06  3876,22  872,056  733,297  473,372 | 359,46  605,581  44,068  81,9883  116,334  87,8316  34,8127  325,795  99,39 |

We note the appearance of one of the bands in the interval from 3700 to 4300 Cm-1with high intensities, which correspond to the O-H Stretch (an unbound free valence frequency). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1[33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**d. H+(H2O)4 :**

The optimization of an**H+(H2O)4** ion by the different levels by the final structure, we have calculated the frequency represented in Table III.26.

Table III.26: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the H+**(H2O)4**  structure with a C3v symmetry

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  H..(H-O-H) Out of plane donor bend | 38787,4  3524,51  3624,1  3112,5  3295,3  3621,2  3985,4  3521,6  3951,2  3651,8  754,25  628,3  698,2 | 48,65  254,12  988,24  52,124  852,.32  941,3  223,69  255,69  354,1  298,3  299,24  917,2  751,08 | 3965,39  4001,44  4016  4030,45  4224,91  4226,66  4230,26  4235,27  3698,1  3254,6  872,102  719,71  714,07 | 0, 7499  786, 945  739,799  14,5301  156,941  127,873  138,258  125,403  254,6  258,4  2,2152  243,44  443,937 | 3396,21  3488,55  3503,44  3544,49  3912,27  3917,45  3920,56  3932,38  3952,24  3658,28  610,338  637,914  643,569 | 81,6559  1390,7  1306,63  206,17  108,599  90,6798  78,9348  101,125  25,85  654,87  88,8322  154,741  200,21 |

We note the appearance of one of the bands in the interval from 3700 to 4300 Cm-1 with high intensities, which correspond to the O-H Stretch (an unbound free valence frequency). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1 [33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**III .3.2.3.** System **(-OH)(H2O)n, with (n = 0..5)**

**a.** **HO- :**

The optimization of aHO- ion at the different levels for the final structure, we calculated the frequency see Table III.27

Table III.27: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the HO- structure with CV. symmetry.

**Tableau III.27 :** fréquence vibrationnel harmonique (Cm-1) et intensités infrarouge (Km/Mol) de la structure HO- avec une symétrie CV.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch | 3826, 71 | 16, 7523 | 4051, 79 | 18, 752 | 4031, 2 | 12, 8448 |

We note the appearance of a single band in the interval from 3800 to 4100 Cm-1, of the hydroxide ion which corresponds to O-H Stretch (frequency of unbound free valence). The latter is located in the red zone. By a comparison with the experimental values 3556 Cm-1[30] we deduce that this value is closer to the value 3826.71 Cm-1 calculated by the MP2 method compared to the two methods DFT and HF.

**b. HO-(H2O) :**

The optimization of an **HO-(H2O)** ion by the different levels by the final structure, the frequency represented in Table III.28 was calculated.

Table III.28: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the HO-**(H2O)**  structure with a C3v symmetry

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  H..(H-O-H) Out of plane donor bend | 3802 ,62  3838 ,22  3995 ,16  416 ,227 | 25 ,1754  61 ,110  122,06  3 ,811 | 3275,39  4151,44  3966  398,502 | 54,6  85,42  98,4  5,241 | 3696 ,45  3742,06  3907,45  415,862 | 30,028  99,064  106,719  3,981 |

We note the appearance of one of the bands in the interval from 3700 to 4300 Cm-1 with high intensities, which correspond to the O-H Stretch (a frequency of unbound free valence). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1[33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**c. HO-(H2O)2 :**

The optimization of a **HO-(H2O)2** ion by the different levels by the final structure, the frequency represented in Table III.29 was calculated.

Table III.29: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the HO-**(H2O)2**  structure with a C3v symmetry

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  H..(H-O-H) Out of plane donor bend | 3607,78  3731,5  3784,99  3971,42  3977,18  636,16  493,621  457,524 | 257,572  254,514  188,011  119,387  138,111  441,702  242,187  66,3285 | 3929,05  4066,79  4102,32  4243,23  4247,26  779,019  577,547  452,796 | 233,374  179,586  135,107  154,385  165,063  11,337  495,314  246,767 | 3392,4  3606,4  3666,47  3898,09  3899,63  679,875  537,4  483,784 | 346,384  327,227  321 ,095  118,75  84,2733  405,592  262,236  119,249 |

We note the appearance of one of the bands in the interval from 3700 to 4300 Cm-1 with high intensities, which correspond to the O-H Stretch (a frequency of unbound free valence). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1[33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**d. HO-(H2O)3:**

The optimization of a **HO-(H2O)3** ion by the different levels by the final structure, the frequency represented in Table III.30 was calculated.

Table III.30: Harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the **HO-(H2O)3**  structure with a C3v symmetry.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  H..(H-O-H) Out of plane donor bend | 38787,4  3524,51  3624,1  3112,5  3295,3  3621,2  3985,4  3521,6  3951,2  3651,8  754,25  628,3  698,2 | 48,65  254,12  988,24  52,124  852,.32  941,3  223,69  255,69  354,1  298,3  299,24  917,2  751,08 | 3965,39  4001,44  4016  4030,45  4224,91  4226,66  4230,26  4235,27  3698,1  3254,6  872,102  719,71  714,07 | 0, 7499  786, 945  739,799  14,5301  156,941  127,873  138,258  125,403  254,6  258,4  2,2152  243,44  443,937 | 3396,21  3488,55  3503,44  3544,49  3912,27  3917,45  3920,56  3932,38  3952,24  3658,28  610,338  637,914  643,569 | 81,6559  1390,7  1306,63  206,17  108,599  90,6798  78,9348  101,125  25,85  654,87  88,8322  154,741  200,21 |

We note the appearance of one of the bands in the interval from 3700 to 4300 Cm-1 with high intensities, which correspond to the O-H Stretch (a frequency of unbound free valence). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1[33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**e. HO-(H2O)4 :**

The optimization of a **HO-(H2O)4** ion by the different levels by the final structure, the frequency represented in Table III.31 was calculated.

Table III.31: harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the HO-(H2O)4 structure with a C3v symmetry

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MP2 | MP2 | HF | HF | DFT | DFT |
| Description | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) | (cm -1 ) | Internsities  (km/mol) |
| O-H Stretch  H..(H-O-H) Out of plane donor bend | 38787,4  3524,51  3624,1  3112,5  3295,3  3621,2  3985,4  3521,6  3951,2  3651,8  754,25  628,3  698,2 | 48,65  254,12  988,24  52,124  852,.32  941,3  223,69  255,69  354,1  298,3  299,24  917,2  751,08 | 3965,39  4001,44  4016  4030,45  4224,91  4226,66  4230,26  4235,27  3698,1  3254,6  872,102  719,71  714,07 | 0, 7499  786, 945  739,799  14,5301  156,941  127,873  138,258  125,403  254,6  258,4  2,2152  243,44  443,937 | 3396,21  3488,55  3503,44  3544,49  3912,27  3917,45  3920,56  3932,38  3952,24  3658,28  610,338  637,914  643,569 | 81,6559  1390,7  1306,63  206,17  108,599  90,6798  78,9348  101,125  25,85  654,87  88,8322  154,741  200,21 |

We note the appearance of one of the bands in the interval from 3700 to 4300 Cm-1 with high intensities, which correspond to the O-H Stretch (a frequency of unbound free valence). These bands are located in the red zone. Appearance of deformation bands in the range of 1000 to 600 Cm-1 which correspond to deformation frequencies. These are located in the blue area. By a comparison with the experimental values 3385 and 3490 Cm-1[33] we deduce that the experimental values correlate well with the frequency values calculated for the different levels.

**III.3.2.4.** System **(-OH,H3O+)(H2O)n With (n = 0, 1, 3)**

**a.** Neutral complex **(-OH, H3O+):**

The optimization of the complexes (-OH, H3O+) for the different levels of the final structure, the frequency represented in Table III.32 was calculated.

Table. III.32: Harmonic vibrational frequency (Cm-1) and infrared intensities (Km/Mol) of the structure(-OH, H3O+) with C1 symmetries.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Systhéme | MP2  (cm -1 ) | MP2  IR  Intensities  (km/mol) | HF  (cm -1 ) | HF  IR  Intensities  (km/mol) | DFT  (cm -1 ) | DFT  IR  Intensities  (km/mol) | Data Experimental  (cm -1 ) |
| Intramolecular            Intermolecular | Acceptor asymmetric O-H Stretch  Donor free O-H Stretch  Acceptor symmetric O-H Stretch  Donor bridge H Stretch  H3O+ donor bend  -OH acceptor bend  H..(H-O-H) Out of plane donor bend  In- plane donor wag  O-O stretch  Acceptor bend  Acceptor twist  Donor torsion | 4000, 68  3978, 55  3861, 32  3788, 01  1658,37  1636,92  676, 401  372, 019  202, 215  178, 67  170, 78  144, 827 | 95, 8597  124, 758  14, 244  260, 284  64, 9643  109, 655  192, 918  128, 61  172, 523  67, 7546  129, 816  143, 051 | 4257, 29  4244, 24  4141, 42  4096, 08  1758, 94  1743, 95  630, 804  359, 79  186, 384  167, 948  157, 579  137, 783 | 121, 565  146, 707  29, 0664  213, 66  92, 7181  135, 431  232, 658  140, 984  248, 51  78, 2911  87 , 4746  136, 708 | 3924, 24  3898, 78  3808, 5  3696, 96  1631, 95  1616, 03  681, 336  393, 602  205, 659  179, 521  170, 518  144, 128 | 86, 8857  95, 0156  13, 9001  332, 356  46, 8163  123, 793  171, 814  97, 2357  198, 959  35, 652  128, 775  182, 66 | **3490c**  **3385c** |

cReference **[¶ 33]**,

The vibrational study of these complexes with the different methods HF, MP2 and DFT was carried out by the base 6-31+G\*\*, see (Table.III.32). This table has been divided into two parts the first represents , intramolecular vibrations and the second intermolecular vibrations. To explain this band we chose the HF method, the appearance of three frequency bands (137-630, 1743-1758, 4096-4257) Cm-1 of varying intensities the first two frequency bands correspond to intramolecular vibrations, the third band corresponds to intermolecular vibrations, the frequency band (4096-4257) Cm-1 corresponds to O-H Stretch vibrations, the band (1743-1758) Cm-1 corresponds to deformation vibrations (bending), and the band (137-630) Cm-1 corresponds to intramolecular vibrations of the O-H bond of the hydrogen bridge O-H..O. A comparison with the experimental values 3385 and 3490 Cm-1 [33] reflects the calculated frequency values.

**b.** Neutral complex **(-OH, H3O+)( H2O):**

The optimization of the complexes (-OH, H3O+)( H2O) for the different levels in the final structure, the calculation of the frequencies is represented in Table III.33

Table. III.33: Harmonic vibrational frequency (cm-1) and infrared intensities (Km/Mol) of the structure (-OH, H3O+)( H2O) with symmetry

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Systhéme | MP2  (cm -1 ) | MP2  IR  Internsities  (km/mol) | HF  (cm -1 ) | HF  IR  Internsities  (km/mol) | DFT  (cm -1 ) | DFT  IR  Internsities  (km/mol) | Data Experimental  (cm -1 ) |
| (-OH, H3O+)( H2O)  (-OH, H3O+)(H2O)3 | 3969, 37  3967, 98  3964, 63  3730, 38  3722, 19  1653, 42  1649, 01  861.006  700, 657  565, 813  347, 639  259, 698  210, 193  192, 581  451, 07  3775,99  3722,56  3712,24  3708,41  3667,24  1651,57  1648,81  897.157  760.545  668.238  641.291  598.752  404,899  380,691  213,472  226,801  193,942 | 121, 161  111, 378  110, 833  405, 507  444, 006  116, 771  132, 572  19.3183  455, 086  179, 755  124, 807  42, 5834  180, 261  12, 1642  150, 232  693,479  143,642  627,636  184,877  287,406  143,642  115,974  29.0476  412.5  417.687  24.0444  267.709  115.238  162,138  122,684  165,693  144,634 | 4426, 65  3980, 03  3945, 8  3942, 27  3677, 15  1828, 27  1757, 69  915, 145  834, 851  719, 518  648.401  617, 83  583, 861  371, 754  276, 676  423994  4237,5  4127,91  4063,3  4036,96  1790,09  1751,9  833.038  811.627  696.731  608.95  566.166  534.352  473,519  366,969  205,617  237,448  180,813 | 946, 269  140, 362  27, 3588  93, 1109  633, 836  196, 862  74, 0879  317, 613  319, 188  53, 503  147.529  126, 958  199, 244  55, 4202  8, 2816  191,149  189,00  517,08  453,999  199,898  22,4773  174,096  106.803  4.2433  512.902  461.502  19.4118  263.968  142,43  137,189  70,304  11,1279  67,7975 | 3899.19  3898.01  3893.22  3616.28  3603.68  1631.08  1626.48  912.853  722.42  604.778  473.567  380,.945  270, 584  250, 727  177, 446  3896.98  3895.4  3894.05  3644.82  3597.31  3592.66  1431,06  779.342  690.921  670.105  633..506  572.159  430.787  416,043  386,379  270, 584  250, 727  198,492 | 57.2785  106.036  97.4185  541.255  596.1  111.833  117.6  16.1281  428.2  213.997  153.197  50.2188  32, 195  64, 5898  120, 171  60.5471  130.992  126.164  832.215  535.396  965.33  186,177  439.353  32.6021  288.214  155.281  161.968  25,2856  145,337  386.622  13,8428  32, 195  21,3725 | **3490c**  **3385c**  **3025d**  **2800e**  **2700f**  **2600f** |

cReference **33**, dReference **35**

eReference **37**, fReference **34**, gReference **36**

The calculation of the frequencies of vibration in these complexes, gives again the frequency bands in the same interval, but with different intensities and the band (277-870) Cm-1 corresponds to the intramolecular vibrations of the bond O-H of the hydrogen bridge O-H..O. with three frequencies (648.401, 617, 83, 583, 861) Cm-1 responding to the three hydrogen bonds of the hydrated complex.

.

**c.** Neutral complex **(-OH, H3O+)(H2O)3:**

he optimization of the complex (-OH, H3O+)(H2O)3 for the different levels by the final structure, the calculated frequencies are in Table III.33.**.**

The calculation of the vibration frequencies in these complexes, gives a band (181-840) Cm-1 which corresponds to the intramolecular vibrations of the O-H bond of the hydrogen bridge O-H..O with six frequencies (534.352, 566.166, 608.95, 696.731, 811.627, 833.038) Cm-1respond to the six hydrogen bonds of the hydrated complex and which can be explained by the number of hydration ligands and their positions (symmetry complex) quite simply the influence of hydration is of great interest on the structure of the complex (-OH, H3O+).

**III.3 3** Influence of coordinates on cantal ions in clusters**:**

**a. structures :**

The number and the position of the coordinates influences the ion cantals by a destabilization of the energy because the interactions inter and intramolecular change, these last influence the stabilization of the structure of complexes, one presents on the table1 various interactions inter and intramolecular on the various complexes studied. Table.III.34: Calculations of the intra and intermolecular coordinates of the neutral complexes**(-OH, H3O+)(H2O)n** and compare them with the experimental values **.**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| HF MP2 DFT Data Experimental a | | | | | | | |
|  | n= 0 n=1 n=3 | | n= 0 n=1 n=3 | | n= 0 n=1 n=3 | |  |
| Intermolecular  R(O-O) [Å]  R(O…H-O) [Å]  a ψ(H-O…H)  Intramolecular  b ψ(H-O-H) °.  R(O-H)c [Å]  R(O-H)d [Å] | 2, 834051 2, 88729 2, 903923  2, 001234 2, 0341 2, 049134  55, 9870 148, 3984 107, 637      117, 1385 91, 679 98, 815  107, 1385 107, 588 107, 869  114, 8552 129, 6005 132, 895  0, 94417 0, 9508 0,959813  0, 94423 0, 9427 0, 960  0,96353 0, 95892 0, 97123  0, 94244 0, 9424 0, 962013 | 2, 914357 2, 79677 2, 805479  2, 009184 1, 9194 2, 03678  55, 2015 147, 363 107, 574  115, 2018 91, 6705 92, 3665  105, 679 106, 476 106, 714  116, 0936 127, 810 131, 338    0, 9643 0, 9751 0, 98345  0, 9643 0, 963 0, 963  0, 97561 0, 9612 0, 9749  0, 9624 0, 9627 0, 9758 | | 2, 889690 2, 78975 2, 785082  1, 923828 1, 8834 2, 040007  53, 5312 149, 38 107, 9534  112, 3741 90, 951 97, 15347  106, 0589 106, 914 106, 951  113, 1782 124, 22 130, 548  0, 9658 0, 9801 0, 985645  0, 9658 0, 9643 0, 972  0, 96586 0, 983 0, 984084  0, 9642 0, 964 0, 98017 | | -  -  104.5 a  104.5 a  111,2 a  0, 950 a  1, 017± 0.005b  1, 01± 0.01c  0, 964 a  1, 017±0.005b  1, 01±0.01c | |

a Angle antre les deux ions ψ(O-H…O)

b Angle de lion H3O+

c Distance de lion H3O+

d Distance de lion OH-

aReference **29**

bReference **31**

cReference **32**

adding a water molecule to see its influence on the neutral complex (-OH,H3O+) . The system formed (-OH,H3O+)(H2O) stabilizes with C1 symmetry. It can be seen that there is a decrease in O-O distance by a value of approximately 0.12 Å, and the hydrogen bond distance d about 0.19 Å, there is a large increase in the O-H bond of the H3O+ ion with a value of about 0.035 Å, and an increase in the angle of the H3O+ ion with a value of about 6°.even (Table.III.34).

Finally, three molecules of water are added to the neutral complex (-OH,H3O+) to study the inter and intramolecular interaction of the system (-OH,H3O+) (H2O)3, we notice a slight increase in the distance R O-O of 0.02 Å with a slight increase in hydrogen bonding distance of 0.21 Å. There is a decrease in O-H bond compared to the first by a value of 0.01 Å with a decrease in angle compared to the first by a value of 2°. See (Table.III.34).

**III.7 Conclusion :**

A comparative structural and energetic inter and intramolecular study by different MP2, HF, DFT levels with the bass 6-31+G\*\* on neutral systems (-OH, H3O+)(H2O)n

The analysis of the results allowed us: to determine the configurations of the coordinates which represent the neutral complexes (-OH, H3O+)(H2O)n.

The addition of a molecule of water to the complex (-OH, H3O+), we notice a significant increase in the O-H bond of the H3O+ion, the same remark concerns the systems

(-OH)(H2O)n, with (n = 0..5), (H3O+)(H2O)n with (n = 0..5), (H+)(H2O)n with (n = 0..5). In the comparative study of the hydrogen bond distance from a donor monomer to the acceptor monomer in the different neutral complexes, it is noted that the O….H distance has decreased, by the addition of three molecules of water to the complex in the different systems to study; and the energy of the latter weakens more and more by the addition of water molecule to the complexes. This finding is predicted by vibrational frequencies. We have studied the

CCl4 (H2O)nsystems with (n = 0..4), to see the influence of the solute on the solvents water or the acidic or basic medium deduces that the solute is very sensitive to environments .

.

It is concluded that this study has provided us with information on the structure, the number of hydration coordinates and the nature of the bonds of the neutral complexes and that the results found give an excellent agreement with the experimental values.

**General conclusion**

A comparative structural and energetic inter and intramolecular study by different MP2, HF, DFT levels with the bass 6-31+G\*\* on neutral systems (M-+)(H2O)n.

The analysis of the results allowed us: to determine the configurations of the coordinates which represent the neutral complexes (M-+)(H2O)n.

The addition of a water molecule to the complex (-OH,H3O+), we notice a significant increase in the O-H bond of the H3O+, ion, the same remark concerns the systems

(-OH)(H2O)n, with (n = 0..5), (H3O+)(H2O)n with (n = 0..5), (H+)(H2O)n with (n = 0..5). In the comparative study of the hydrogen bond distance from a donor monomer to the acceptor monomer in the different neutral complexes, it is noted that the O….H distance has decreased, by the addition of three molecules of water to the complex in the different systems to study; and the energy of the latter weakens more and more by the addition of water molecule to the complexes. This finding is predicted by the frequencies of vibration.

It is concluded that this study has provided us with information on the structure, the number of hydration coordinates and the nature of the bonds of the neutral complexes and that the results found give an excellent agreement with the experimental values.

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