STUDY OF HYDROGEN-BONDED COMPLEXES USING *AB-INITIO* CALCULATIONS

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ABSTRACT

In this work the vibration frequencies of the formamide molecule C=O and N–H were investigated on the basis of the method of density function theory (DFT) and a set of bases B3LYP/6-311++G(2d, p) and also geometric and optical parameters of molecules were studied. Theoretical calculations have shown that that the C=O and N–H vibration bands of formamide shown shifted towards low frequencies in the formation of molecular aggregates. As the amount of water in the solution increases, the energy of aggregate formation increases. Aggregates were formed by different types of H-bonds. Calculations have shown that as the amount of water increases, H-bonds are formed not only through O-H⋯O, but also through O-H⋯N-type non-classical bonds. Density distributions and 3 D potential energy graphs for formamide and water systems were also studied. This allows us to learn more about the intermolecular interaction energies in the formamide aquatic environment.

KEYWORDS:*Formamide; Raman Spectra; H-Bond; Vibration Spectrum; Frequency; Simulation.*

INTRODUCTION

The study of the processes that occur among atomic particles aids in the knowledge of the concept of molecular interactions, and the scientific validation of such interactions gives knowledgeabout rise to life. Today, in the field of physics, chemistry and biology, the results obtained through theoretical calculations, as well as experimental studies on various molecular compounds, are widely used. The ease of theoretical calculations allows the identification of parameters that are difficult to determine in an experiment and the achievement of new results. **[1-4].** One of the simplest representatives of biological substances is formamide, a clear liquid amide, composed of four essential elements: carbon, hydrogen, oxygen, and nitrogen bound to the peptide. Any information about the electronic structure and geometry of this molecule is important in protein chemistry and physics **[5, 6].**

Understanding the role of water in biological systems necessitates research into the interaction of formamide with water. Aqueous solutions of formamide have been studied by many researchers **[7-11].**Understanding the nature and features of such interactions allows us to draw conclusions about the structure and spectrum manifestations of biomolecules. Also Almerindo and Pliego Jr. in the aqueous solution of the formamide molecule using calculations in the set of bases CCSD(T)/6-311+G(2df,2p), MP2/6-31G(d), B3LYP/6-311+G(2df,2p)the activation energy was calculated and the accuracy of the calculations in the set B3LYP/6-311+G(2df, 2p) was found to be high **[9].** The cyclic structure of the formamide-water complex, semi-classical formulas of internal and intermolecular energies and solutions of equations of motion are studied **[11].** Similarly, calculations were made at 6-311G approximation of formamide with 5 water and the energies were compared in different methods **[12].** The physical processes that occur as a result of vibrational processes in the formamide water system have not yet been fully studied. Therefore, an attempt was taken in this work in using theoretical calculations to investigate the nature of the intermolecular forces that occur in formamide and its aqueous solutions. In this case, we studied $C = O$, and $N - H$ of the vibration frequencies of the formamide molecule on the basis of the method of density function theory (DFT) and a set of bases B3LYP//6-311++G(2d, p).

CALCULATION RESULTS

In our previous work, the Raman spectrum of the C=O vibration of formamide and its various aggregates with dimethyl sulfide oxide were studied using experimental and theoretical calculations **[12].** Also in our recent work, the geometric optimization of molecular complexes in aqueous solutions of formamide molecules studied in 3 different ways: Hartree-Fock (HF), density function theory (DFT) and the second order Møller–Plesset(MP2) pertrubation theory studied on the set of bases 6-311++G(2d,p) **[13].** Charge density distributions and three-dimensional potential energy graphs for formamide and water systems were also examined in this work. This allows us to learn more about the energies of intermolecular interactions.The density function theory(DFT) was used to perform quantum chemical calculations in Gaussian 09 utilizing a set of bases(B3LYP)/6-311++G(2d, p) **[14, 15].** In **[13],** calculations were performed for different aggregates of the formamide molecule with water. Figure 1 shows the result calculated on the basis of density function theory (DFT) for aggregates of molecular complexes of water up to 6 hexamers with 1 molecule of formamide. Figure 1a shows the dimers of the formamide and water molecules, forming an H-bond between the O3 atom of the formide

and the H9 atom of water, and a hydrogen bond with a binding energy of 0.85 kcal / mol. When the calculations were continued by increasing the value of water by one more, the number of these hydrogen bonds reached three. The H-bond energy is 1.99 kcal / mol, with two bonds formed by O-H⋯O, and a third bond formed by O-H⋯N bonds, which are weak with the nitrogen atom of formamide. The literature also states that the O-H⋯N bridge is weaker than the O-H⋯O bridge **[16].**

Figure 1b shows 1 formamide and 3 water aggregates. There are 4 hydrogen bonds with an energy of 3.14 kcal/mol and all the bonds are formed by O-H⋯H s. Similarly, the calculations show that when the number of water molecules is increased to 4, the energy is 4.44 kcal/mol and the number of hydrogen bonds is 5, 1 of which belongs to the O-H⋯N nonclassical bond, as mentioned above.

kkal/mol
E=3.14 kkal/mol

a)
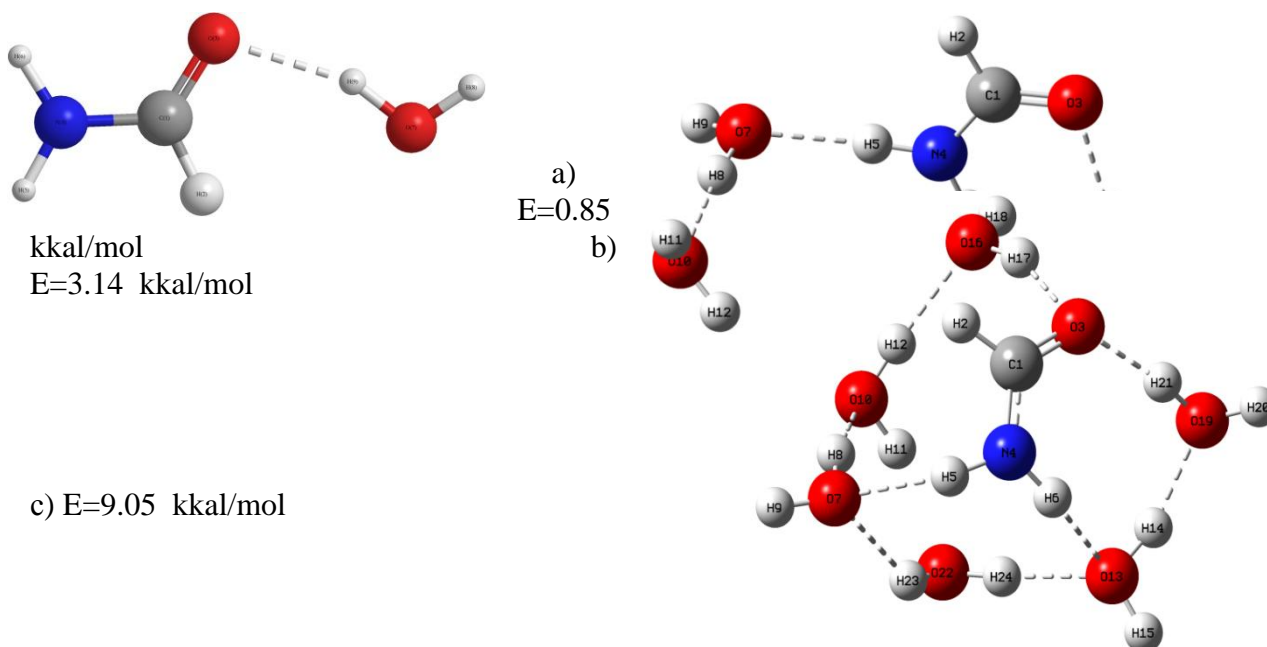E=0.85

b)

c) E=9.05 kkal/mol

Figure 1. Aggregates of formamide formed with water. a) F + 1W, b) F + 3W, s) F + 6W

When the value of water was increased 5 and 6 (Fig. 1 s), the energies were 6.98 and 9.05 kcal/mol, respectively and all bonds closed structural aggregates formed through the O-H⋯O bond.The electro-optical parameters of the molecule found using theoretical calculations (Tables 1-3) are given. Table 1 shows the charge distributions for the systems formed by the formamide molecule with water.

TABLE 1. MULLIKEN CHARGE DISTRIBUTION WHEN FORMAMIDE FORMS A CLUSTER WITH WATER

Structure	C1	H2	O3	N4	H5	H6
F	0.25	0.06	-0.46	-0.32	0.23	0.23
F+1W	0.29	0.08	-0.52	-0.37	0.25	0.29

F+2W	0.26	0.08	-0.59	-0.52	0.34	0.25
F+3W	0.27	0.09	-0.54	-0.45	0.37	0.28
F+4W	0.26	0.12	-0.45	-0.57	0.33	0.29
F+5W	0.28	0.13	-0.63	-0.42	0.31	0.36
F+6W	0.18	0.15	-0.56	-0.38	0.30	0.31

The charges of the formamide molecule have changed, and this change is greater in the atoms involved in hydrogen bonding.Table 2 shows the change in the chemical bond lengths of the fomamide molecule, and as mentioned above, the change in bond lengths is also greater in the atoms involved in hydrogen bonding. The results obtained are confirmed in the reference **[17].**

TABLE 2. BOND LENGTHS WHEN FORMAMIDE FORMS A CLUSTER WITH WATER. (Å)

Structure	O3-C1	C1-H2	C1-N 4	N4-H6	N4-H5
F	1.21	1.11	1.36	1.01	1.01
F+1W	1.22	1.10	1.35	1.02	1.01
F+2W	1.21	1.11	1.37	1.01	1.02
F+3W	1.23	1.10	1.34	1.02	1.02
F+4W	1.23	1.10	1.35	1.02	1.02
F+5W	1.24	1.09	1.32	1.03	1.01
F+6W	1.24	1.09	1.33	1.02	1.02

Table 3 shows the frequencies calculated using formamide calculations for the vibration C=O, which matched to a frequency of 1770 cm^{-1} in the experiment.As can be seen from the table, as the value of water increases, the frequency shifts downward. The table also shows the dipole moments, the values of the dipole moments decrease as the number of molecules increases, but partially increased when the number of water molecules is 3, which can be seen from Figure 1b due to the formation of an open chain of molecules. Similarly, Table 3 shows the total vibration energy and intermolecular interaction energies of the molecule.

TABLE 3. THE RESULTS OF CALCULATIONS FOR MOLECULAR CLUSTERS OF FORMAMIDE (F) AND WATER (W) MOLECULES

Structure	Frequency of C=O vibration , cm^{-1}	Dipole moment, D	Energy of vibration, kkal/mol	Energy of intermolecular interaction, kkal/mol
F	1782.8	4.02	28.28	-
F+1W	1758.6	4.09	43.58	0,85
F+2W	1752.8	3.78	59.17	1,99
F+3W	1738.6	5.21	74.76	3,14

F+4W	1743.3	3.40	90.50	4,44
F+5W	1729.0	1.46	107.50	6,98
F+6W	1735.9	3.80	124.01	9,05

The table shows that as the number of water molecules increases, the value of energy increases. In this case, just like the value of the dipole moment, the formamide molecule combines with 3 water molecules to reduce the energy value slightly, and such a decrease can be explained by the formation of an open chain in the formation of the aggregate.
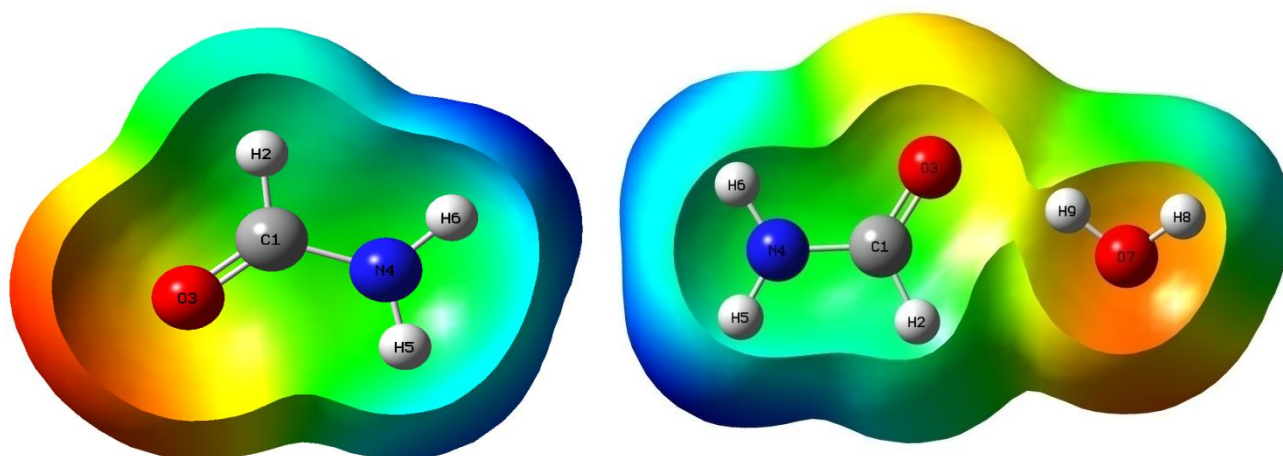
Figure 2. Charge density distribution of formamide and formamide-water

Figure 2 shows its electrostatic potential through the electron density distribution of atoms in a formamide molecule. Electrostatic potential surfaces characterize the molecular size, shape, charge density, and chemical reactivity properties. Depending on the level of electrostatic potential, it is expressed in different colors. The orange<yellow<green<blue order shows the increase in electrostatic potential.As can be seen from the figure, C=O indicates that the surface around the bond is orange, i.e., it has the smallest potential, while N-H is blue, which indicates that it has the largest electrostatic potential.
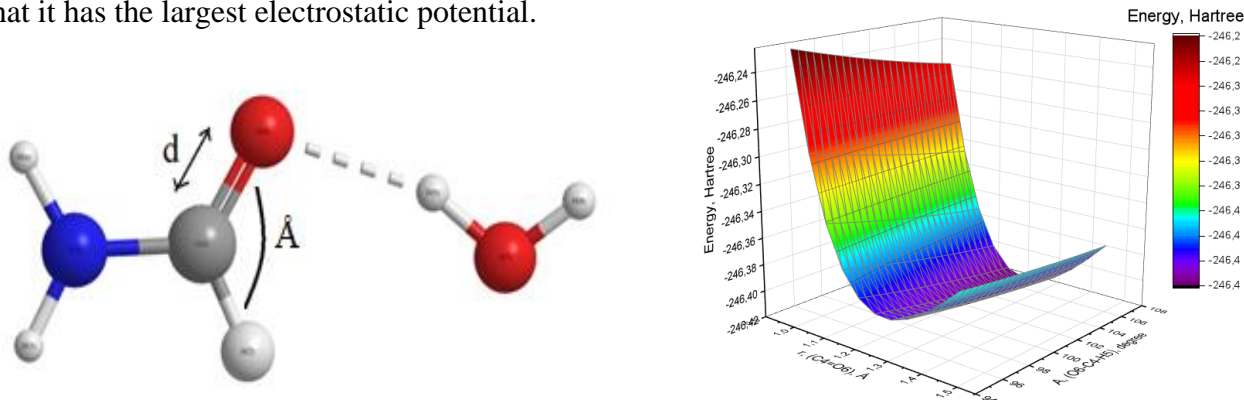

Figure 3. 3 D potential energy graph for formamide water system

Figure 3 shows the aggregation of formamide-water molecules and a 3D graph of the potential energy dependence of its angle (between O6-C4-H5) and distance (between C4=O6). The calculations show that the energy of the molecule being optimized is the distance between the atoms (1.0 to 1.5 Å) and the angle (94 to 108 ^{0}), respectively. The lower part of the graph shows that the optimized energy corresponds to known intervals, rather than the exact discrete value of distance and angle.

CONCLUSION

Calculations show that the formamide molecule forms different aggregates with the water molecule and can consist of several types. In particular, there are aggregates of formamide with H atoms of the NH_2 group, as well as aggregates of formamide with the oxygen atom of the C = O group and the H atom of the O–H group of water. An increase in the amount of water in the aggregates of formamide + water molecules resulted in the formation of open and closed type complexes of different types of H-bonds. Also, as the amount of water in the solution increases, the energy of complex formation also increases.

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