COMPUTATIONAL INVESTIGATION OF HYDROGEN-BONDED COMPLEXES USING AB INITIO METHODS

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ABSTRACT

In this study, the vibrational characteristics of the C=O and N–H groups in the formamide molecule were investigated using density functional theory (DFT) at the B3LYP/6-311++G(2d,p) level of theory. In addition, the geometrical and optical properties of the molecular systems were analyzed. The theoretical results revealed that the C=O and N–H stretching vibrations of formamide undergo red shifts upon the formation of molecular aggregates. An increase in the water content of the system was found to enhance the stability and formation energy of these aggregates. The aggregates are stabilized by various types of hydrogen bonds. The calculations further demonstrated that, with increasing numbers of water molecules, hydrogen bonding occurs not only through conventional O–H···O interactions but also through O–H···N-type interactions. Furthermore, the electron density distributions and three-dimensional molecular electrostatic potential maps of the formamide–water systems were examined. These results provide deeper insight into the nature and energetics of intermolecular interactions in the aqueous environment of formamide.

Introduction

Investigating the processes occurring at the atomic and molecular levels is essential for understanding the nature of intermolecular interactions. The scientific characterization of these interactions contributes to a broader understanding of molecular organization and the fundamental processes underlying the emergence and development of life. Today, both theoretical and experimental approaches are widely employed in physics, chemistry, and biology to study the properties and behavior of various molecular systems. Computational methods are particularly valuable because they enable the determination of molecular parameters that may be difficult or inaccessible to obtain experimentally, thereby providing new insights into the structure and properties of complex molecular systems [1–4].

Formamide is one of the simplest biologically relevant amides and is a colorless liquid composed of carbon, hydrogen, oxygen, and nitrogen. It contains a peptide-like bond, making it an important model compound for investigating fundamental structural and electronic properties relevant to protein chemistry and molecular physics. Consequently, detailed knowledge of its molecular geometry and electronic structure is of considerable interest [5,6].

A comprehensive understanding of the role of water in biological systems also requires detailed investigation of the interactions between formamide and water molecules. Formamide–water mixtures and aqueous formamide solutions have therefore attracted considerable research interest [7–11]. Elucidating the nature and characteristics of these intermolecular interactions can provide valuable information about the structural organization of biomolecular systems and their spectroscopic behavior. For example, Almerindo and Pliego Jr. investigated formamide in an aqueous environment using CCSD(T)/6-311+G(2df,2p), MP2/6-31G(d), and B3LYP/6-311+G(2df,2p) calculations. Their results demonstrated that the B3LYP/6-311+G(2df,2p) level provides relatively high accuracy for calculating the relevant activation energies [9]. In other studies, the cyclic structures of formamide–water complexes, as well as the intramolecular and intermolecular energy contributions and the corresponding equations of motion, have been examined [11]. Calculations involving formamide complexes with five water molecules have also been performed using the 6-311G basis set, and the resulting interaction energies were compared using different computational methods [12].

Despite these previous investigations, the physical processes associated with vibrational behavior and intermolecular interactions in formamide–water systems have not yet been fully elucidated. Therefore, the present study employs theoretical calculations to investigate the nature of the intermolecular forces and hydrogen-bonding interactions in isolated formamide and its aqueous molecular complexes. Particular attention is focused on the vibrational frequencies of the C=O and N–H groups of formamide. These vibrational properties are analyzed using density functional theory (DFT) calculations at the B3LYP/6-311++G(2d,p) level of theory.

Calculation results

In our previous study, the Raman spectral characteristics of the C=O vibrational mode of formamide and its various aggregates with dimethyl sulfoxide were investigated using a combination of experimental measurements and theoretical calculations [12]. In another recent study, the geometries of formamide–water molecular complexes were optimized using three different computational approaches: Hartree–Fock (HF), density functional theory (DFT), and second-order Møller–Plesset perturbation theory (MP2), all employing the 6-311++G(2d,p) basis set [13]. The electron density distributions and three-dimensional molecular electrostatic potential maps of the formamide–water systems were also analyzed, providing additional insight into the nature and energetics of the intermolecular interactions.

In the present work, quantum-chemical calculations were performed using density functional theory (DFT) as implemented in the Gaussian 09 software package, employing the B3LYP/6-311++G(2d,p) level of theory [14,15]. As reported in [13], calculations were carried out for a series of molecular aggregates consisting of one formamide molecule and an increasing number of water molecules. Figure 1 presents the DFT-optimized structures of formamide–water complexes containing up to six water molecules.

Figure 1a illustrates the formamide–water dimer, in which an intermolecular hydrogen bond is formed between the O3 atom of formamide and the H9 atom of a water molecule. The calculated binding energy of this complex is 0.85 kcal mol^{-1}. Upon the addition of a second water molecule, the number of intermolecular hydrogen bonds increases to three, and the corresponding interaction energy reaches 1.99 kcal mol^{-1}. Two of these hydrogen bonds are of the O–H···O type, whereas the third interaction involves an O–H···N hydrogen bond with the nitrogen atom of formamide. This latter interaction is comparatively weak, consistent with previous reports indicating that O–H···N hydrogen bonds are generally weaker than O–H···O interactions [16]. Figure 1b shows the aggregate containing one formamide molecule and three water molecules. In this complex, four hydrogen bonds are formed, with a calculated interaction energy of 3.14 kcal mol^{-1}. The hydrogen-bonding network is mainly established through intermolecular O–H···O interactions. Further increasing the number of water molecules to four leads to the formation of five hydrogen bonds and an increase in the interaction energy to 4.44 kcal mol^{-1}. Among these interactions, one corresponds to the comparatively weak and nonclassical O–H···N hydrogen bond discussed above.

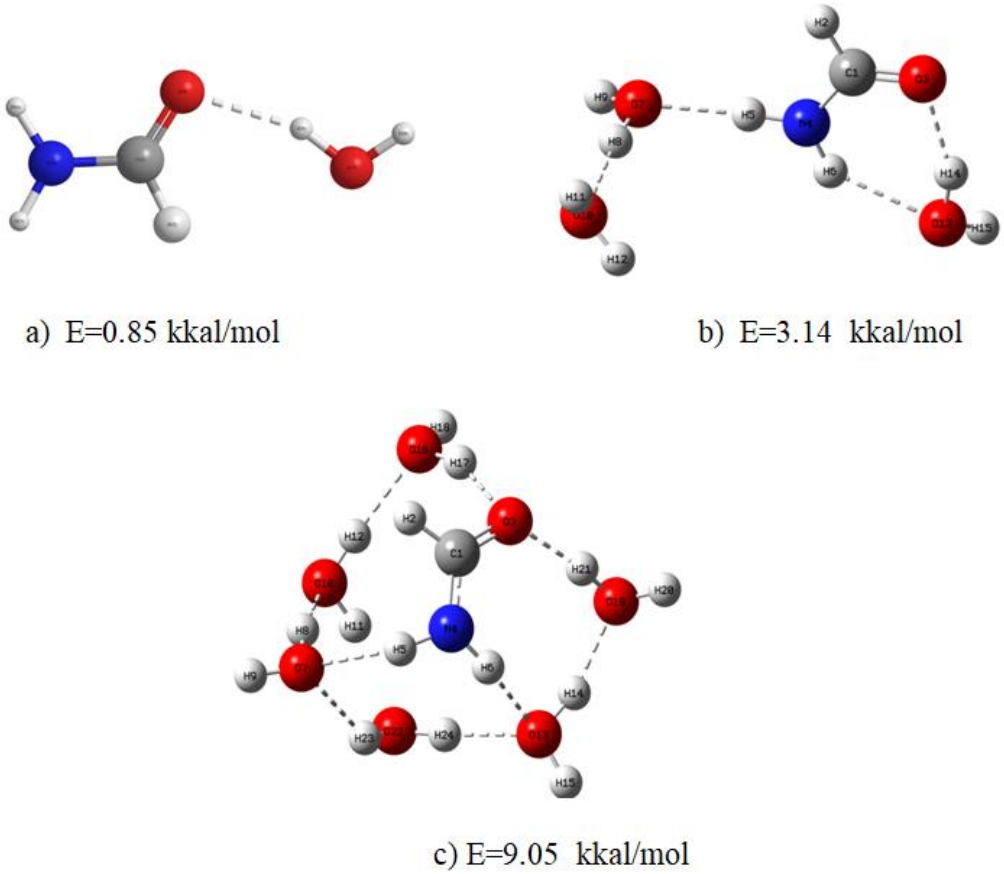


Figure 1. Aggregates of formamide formed with water. a) F + 1W, b) F + 3W, s) F + 6W

Upon increasing the number of water molecules to five and six (Fig. 1c), the calculated interaction energies increased to 6.98 and 9.05 kcal mol^{-1}, respectively. At these hydration levels, closed molecular aggregates are formed, with the intermolecular network stabilized predominantly by O–H···O hydrogen bonds. The electro-optical parameters obtained from the theoretical calculations are summarized in Figure 2 and Tables 1–2. In particular, Figure 2 presents the calculated Mulliken atomic charge distributions for the molecular systems formed

by formamide and water. The calculated atomic charges of the formamide molecule undergo noticeable changes upon complex formation, with the most pronounced variations occurring at the atoms directly involved in hydrogen bonding. Table 1 summarizes the changes in the bond lengths within the formamide molecule. Similar to the charge redistribution, the largest variations in bond lengths are observed for the bonds associated with the hydrogen-bonding sites. These findings are consistent with the results reported in the literature [17].

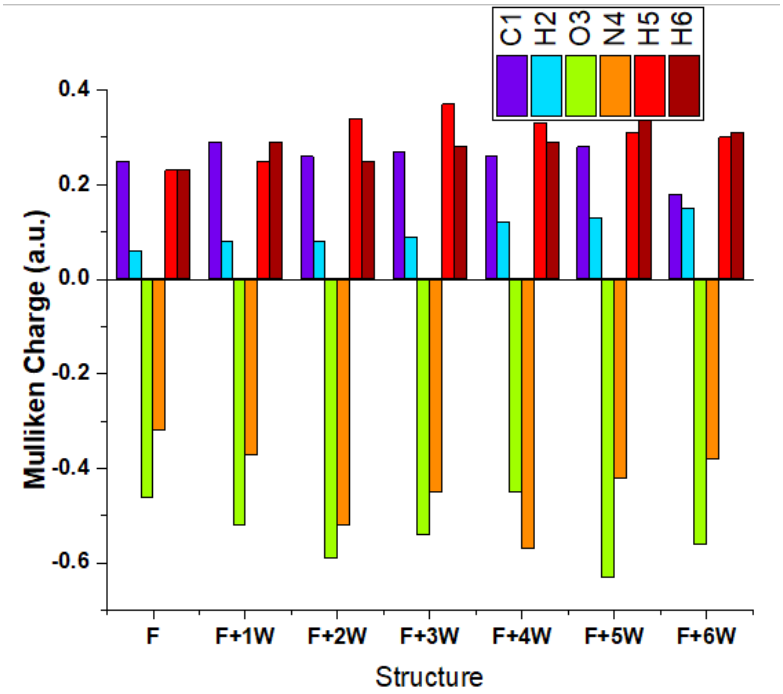


Figure 2. Mulliken charge distribution of formamide–water clusters

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

Table 1. Bond lengths in formamide–water clusters (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 2 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 2 shows the total vibration energy and intermolecular interaction energies of the molecule.

Table 2. Calculated properties of formamide (F)–Water (W) molecular clusters

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 data presented in the table indicate that the interaction energy generally increases with increasing numbers of water molecules in the cluster. However, similar to the behavior observed for the dipole moment, the formamide complex containing three water molecules exhibits a slight decrease in energy. This behavior can be attributed to the formation of an open-chain configuration within the molecular aggregate, which leads to a different arrangement of the intermolecular hydrogen-bonding network.

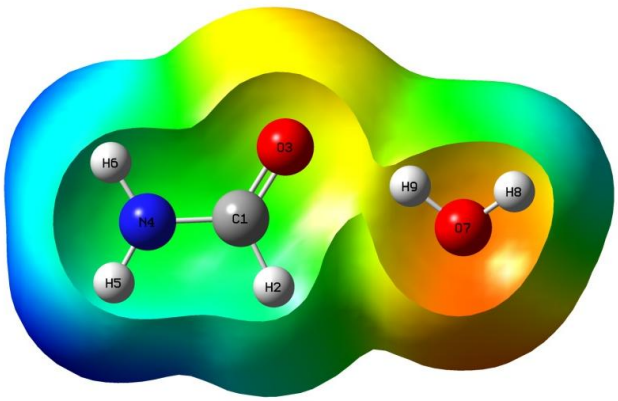
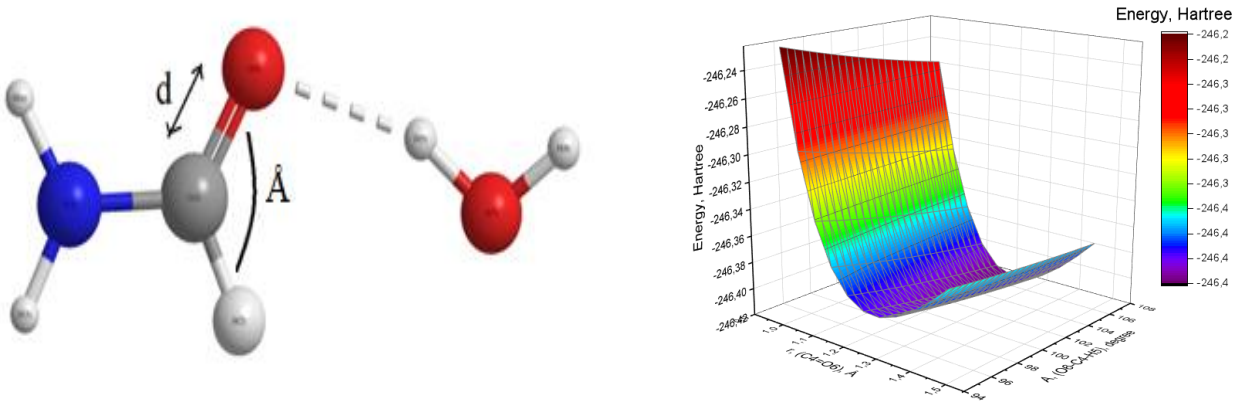


Figure 3. Molecular electrostatic potential maps of formamide–water complexes

Figure 3 presents the molecular electrostatic potential (MEP) maps calculated for the formamide–water complexes. MEP surfaces provide valuable information about the molecular size and shape, as well as the spatial distribution of electrostatic potential, which is closely related to chemical reactivity and intermolecular interactions. The electrostatic potential is

represented using a color scale, where the values increase in the order orange < yellow < green < blue. As shown in Figure 3, the region surrounding the C=O group is characterized by an



orange color, corresponding to a relatively lower electrostatic potential, whereas the N–H region appears blue, indicating a comparatively higher electrostatic potential. These variations in the MEP surface reflect the different electrostatic characteristics of the molecular sites and help identify regions that are favorable for intermolecular interactions.

Figure 4. Three-dimensional potential energy surface of the formamide–water system

Figure 4 illustrates the aggregation of formamide and water molecules together with a three-dimensional potential energy surface describing the dependence of the molecular energy on the O6–C4–H5 angle and the C4=O6 bond distance. The calculations indicate that the optimized molecular configuration is associated with a C4=O6 distance in the range of 1.0–1.5 Å and an O6–C4–H5 angle of approximately 94–108°. The lower-energy region of the surface demonstrates that the optimized structure is not restricted to a single discrete combination of bond distance and angular coordinates. Instead, a range of geometrical parameters can correspond to energetically favorable configurations.

Conclusion

The calculations demonstrate that formamide can interact with water molecules through several distinct aggregation patterns. In particular, hydrogen-bonded complexes may involve the hydrogen atoms of the NH_2 group of formamide, as well as interactions between the carbonyl oxygen (C=O) of formamide and the hydrogen atoms of the O–H groups in water. As the number of water molecules increases, the formamide–water system develops both open- and closed-type molecular complexes stabilized by different hydrogen-bonding configurations. Furthermore, the calculated complexation energy generally increases with increasing water content, indicating stronger overall intermolecular interactions within the hydrated formamide aggregates.

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