

Study Of The Mechanisms Of Formation Of Aggregates In Ethyleneglycol Molecules Using Theoretical Calculations

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Abstract – In this study, theoretical calculations for liquid ethyleneglycol molecule monomer, dimer and trimer molecules were performed on the basis of 3 different HF, MP2 and DFT methods and a set of B3LYP//6-311++G(d,p) bases. Along with the determination of optical and geometric parameters, electrostatic potential surfaces and 3 D graph of the energy dependence to distance and angle was drawn.

Keywords – Ethyleneglycol, DFT, hydrogen bonding, monomer, dimer, trimer, tetramer, bond energy, charge distribution.

I. INTRODUCTION

Hydrogen bonding is one of the forces of intermolecular and intramolecular interactions that is of interest to many scientists. The study of the vibration spectra of such bonded compounds, i.e., the Raman scattering and IR absorption spectra, allows us to solve problems related to the nature, structure, and formation of molecular aggregates. Also, to determine the relationship between experiment and theory [1]. In the study of the structural properties of the molecule ab-initio calculations are currently used. This paper consists of studying the mechanisms of formation of molecular aggregates in ethylene glycol using quantum chemical calculations. Ethylene glycol is widely used in the medical, oil and gas industries, in antifreeze and cooling parts in automobiles, in melting ice formed by wind as a result of wind in aircraft, as a moisturizer for fibers and skin. Therefore, there are unsolved issues in the nature of this substance and require scientific work on it [2,3]. For example, the intermolecular interactions of ethylene glycol and its aqueous solutions have been studied by scientists [4 - 8]. [9-13] studied the nature of the formation of different molecular clusters using the Raman spectra of ethylene glycol as well as quantum chemical calculations. F.H. Tukhvatullin et al [14] studied the formation of monomers and dimers of ethylene glycol using Raman spectra of light and theoretical calculations. In addition, studies [16, 17] have suggested that the bond lengths and atomic charges of the two CH₂OH groups in ethyleneglycol differ from each other. From the above, it can be said that there are unsolved problems in the formation of aggregates of ethylene glycol molecules, and it is important to continue scientific work in this regard.

II. RESULTS AND DISCUSSIONS

In our previous work [2], the process of cluster formation in ethylene glycol molecules and their spectral manifestations were analyzed using Raman spectra and quantum chemical B3LYP calculations. In this study, the mechanisms of cluster formation in ethylene glycol molecules were studied using a number of theoretical computational methods: Hartree Fock (HF) approach, second-order Moller-Plesset excitation theory (MP2), density functional theory (DFT), and molecular mutual orientation, dimer, trimer formation energies, vibration frequencies and bond lengths, charge distribution, and change in angles

were determined. Theoretical calculations were performed on the basis of a set of bases B3LYP//6-311++G(d,p) for isolated monomers, dimers and trimers of ethylene glycol (Fig. 1). Figure 1 (a) shows that in an ethyleneglycol monomer there are 2 intermolecular H-bonds between oxygen and hydrogen atoms (bond lengths 2.027 and 2.093 Å), the dipole moment of the monomer is 2.6 D. Figure 1 (b) shows the dimer of ethylene glycol. In dimer formation, an H-bond is formed between the H10 and O19 atoms (bond length 1,886Å). The energy of dimer formation is 2.30 kcal/mol, the dipole moment is 2.9 D. Three types of hydrogen bonds are involved in the formation of the trimer molecule. The first two occur between the O14, H10, and O9, H25 atoms in the OH groups (bond lengths are 1.82 Å and 1.87 Å, respectively), while the third hydrogen bond is between the O24 and H12 atoms (bond length 2.46 Å). The energy of formation of the trimer is 4.13 kcal/mol, the dipole moment is 5.3 D.

Another achievement of modern theoretical calculations is that it is possible to analyze Raman spectra using these methods. It should be noted that the frequencies of the theoretically determined Raman spectra differ by about 10% from the line frequencies observed in the experiments.

Figure 1 shows the Raman spectra of monomer, dimer, and trimer aggregates of ethylene glycol. As the number of interacting molecules (the number of hydrogen bonds) increases, the frequency peaks shift toward the lower frequency. This trend is consistent with the results of the study in the study [17]. The formation of intermolecular and intermolecular hydrogen bonds in liquid ethyleneglycol is more pronounced in the Raman spectra as the number of molecules in the aggregates increases.

When an H-bond appears in the dimer, three to six additional vibration bands appear in the vibration spectrum.

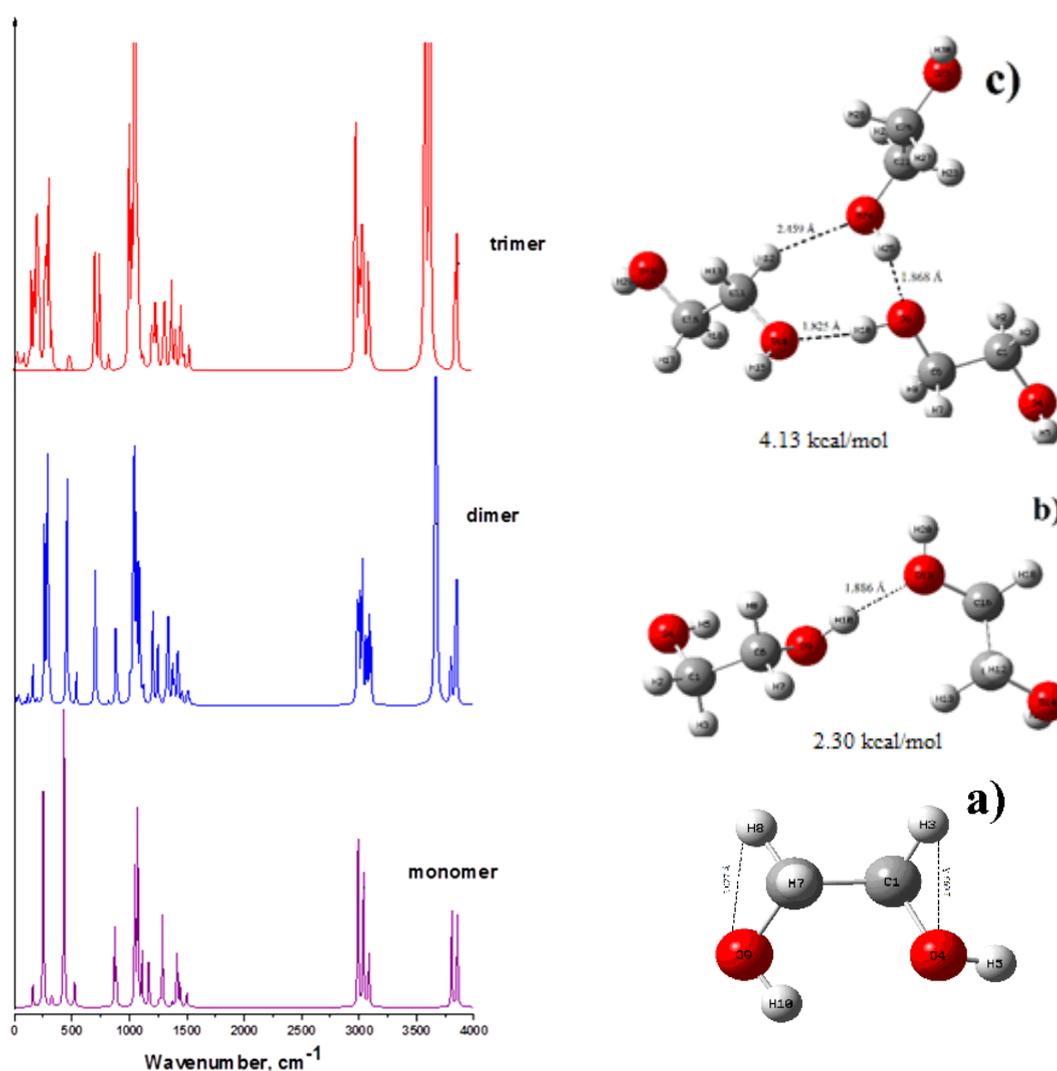


Figure 1. The optimal geometry and spectra of ethyleneglycol obtained in the set of B3LYP/6-311++G(d,p) bases. a) monomer, b) dimer, c) trimer.

These bands are associated with molecular interactions that surround the hydrogen bond. The deformation O-H band obtained in the experiment corresponds to a frequency of 1078 cm⁻¹ band [2]. In the theoretical calculations, 1155 cm⁻¹ (MP2), 1170 cm⁻¹ (DFT) and 1256 cm⁻¹ (HF) bands correspond, respectively. This is close to the experimental results of 1155 cm⁻¹ found by calculations.

Another convenience of theoretical calculations is that the density distribution can be determined. To this end, theoretical calculations were continued. Figure 2 shows a visual representation of electrostatic potential surfaces.

Table 1: Distance (d_{X-Y}, Å), angle (A_{X-Y-Z}, degree), charge (q_X, e) and dipole moment (D) of ethylene glycol monomer calculated by 3 different methods.

| Parameters | Methods | | |
|--|---------|--------|--------|
| | MP2 | DFT | HF |
| d _{O-H} , O ₄ -H ₁₀ | 2.43 | 2.39 | 2.43 |
| A _{H-O-C} , H ₁₀ -O ₉ -C ₆ | 108.64 | 106.87 | 110.77 |
| q _H , H ₁₀ | 0.28 | 0.25 | 0.28 |
| q _O , O ₉ | -0.31 | 0.33 | -0.31 |
| Dipole moment | 2.69 | 2.62 | 2.69 |

Table 2: Distance (d_{X-Y}, Å), angle (A_{X-Y-Z}, degree), charge (q_X, e) and bond energy (kcal/mol) and dipole moment (D) of ethylene glycol dimer calculated by 3 different methods.

| Parameters | Methods | | |
|---|---------|--------|-------|
| | MP2 | HF | DFT |
| d _{O-H} , (O ₁₉ -H ₁₀) | 2.25 | 1.97 | 1.82 |
| A _{H-O-C} , (H ₁₀ -O ₉ -C ₆) | 108.2 | 110.58 | 109.3 |
| q _H , H ₁₀ | 0.30 | 0.45 | 0.42 |
| q _O , O ₁₉ | -0.37 | -0.39 | -0.38 |
| ΔE | 2,62 | 2.11 | 2.30 |

The binding energy (ΔE) is determined by the difference between the energy of the complex (E_{complex}) and the total energy (ΣE_{components}) of each component.

$$\Delta E = E_{\text{complex}} - \Sigma E_{\text{components}} \quad (1)$$

The red part is more negatively charged and the blue part is more positively charged. Electrostatic potential surfaces characterize the size, shape, charge density, and chemical reactivity properties of a molecule. 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.

interval. The calculations show that the distance between the atoms (0.8 Å to 1.3 Å) and the potential energy (in Hartree units) around the angle (80° to 200°) of the molecule being optimized are respectively drawn. In this case, the total number of steps was 275 according to the formula $(m + 1)(n + 1)$ when the calculated distance was 10 (n) steps and the angle was 24 (m) steps. The choice of this distance and angle is due to the fact that the hydrogen bond involved in the formation of the dimer has a large effect on the change of these parts (distance, angle). 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. This interval corresponds to the lowest dark red color, as shown in Figure 3b), and has an energy of -406.7 Hartree. 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. This interval corresponds to the lowest dark red color, as shown in Figure 3 b) and has energy of -406.7 Hartree.

III. CONCLUSION

Calculations have shown that ethyleneglycol molecules form cyclic closed dimers through open-chain dimers and type 3 hydrogen bonds. Dimer formation energy was found to be 2.3 kcal/mol and trimer formation energy was found to be 4.15 kcal/mol.

Ethylene glycol molecules are involved not only in intermolecular interactions, from which an intermolecular hydrogen bond is observed, and an intermolecular hydrogen bond is also maintained in the dimer of the molecule.

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