

[P8] Theoretical study on the structures of ethanolamine and its water complexes using the Hamiltonian algorithm

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Chemical absorption of CO₂ using an aqueous solution of monoethanolamine [MEA, HOCH₂CH₂NH₂] is an important industrial method and has been studied many times both experimentally [1] and theoretically [2].

In these theoretical studies, all-trans configuration was employed, however, MEA has three single bonds in its backbone and clearly has a number of tautomers. In the present study, we try to optimize the structures of MEA, MEA + two water molecules as the model of MEA in aqueous solutions, and MEA dimer. The geometry optimization of MEA itself is easy by using the today's standard molecular orbital program package such as Gaussian09 [3], however, those of MEA + two water molecules and MEA dimer are very difficult without any additional setup. We used the Hamiltonian algorithm [4] as a setup. The Hamiltonian algorithm is useful to find unpredictable structures and we can optimize the structures of complicated molecular complex.

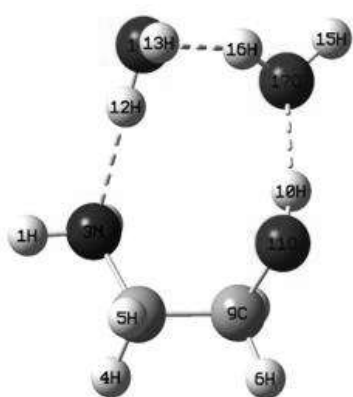


Fig. 1. The optimized structure of MEA + two H₂O.

Gaussian09 [3] and GAMESS [5] program packages are used for the molecular orbital calculations. The optimization by the Hamiltonian algorithm are performed at HF/3-21G level and the geometries are then refined by the optimization at HF/6-31++G** and MP2/6-31++G** levels.

We obtain 13 optimized structures of MEA. The most stable tautomer is a gauche structure as is considered above. Dihedral angles of the H-N-C-C-O-H backbone are calculated to be 79.3, 56.4, and -42.0 degrees, respectively, whereas those of all-trans tautomer are calculated to be 166.6, 176.4, and 172.7 degrees, respectively at MP2/6-31++G** level.

We obtained more than 30 optimized structures of MEA + two water molecules. Although we consider there are more number of configurations, we terminated the calculations within a moderate computational effort. The most stable optimized structure is shown in Figure 1, whose MEA structure is also the gauche structure. The most interesting feature of this structure is the direction of the

hydrogen bond between the hydroxy group and the water molecule. The hydrogen bond is formed between the hydrogen atom of the hydroxy group and the oxygen atom of the water molecule, whereas, in the other optimized structures which are not shown here, the hydrogen bonds are formed between the hydrogen atom of water molecule and the oxygen atom of the hydroxyl group. The hydronium ion is expected to be formed easily by the proton transfer from hydroxyl group to the water molecule in the most stable structure.

Bibliography :

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