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Structure of water molecule and water hydrogen bonding: joint Cambridge Structural Database and *ab-initio* calculations study

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Water molecule is ubiquitous in nature. Due to polar structure and ability for hydrogen bonding water molecule plays important role in many life processes as well as in packing of small molecules crystal structures. Over the past decades, the structure of water molecule [1] and water dimers [2] has been intensively studied. The experimental values for a free water molecule in the gas phase are the bond (O-H) length of 0.9572 ± 0.0003 Å and the bond angle (H-O-H) of 104.52 ± 0.05º. [3] Calculations have showed that equilibrium structure of water molecule has the bond length of 0.95785 ± 0.00005 Å and the bond angle of 104.501± 0.005º. [4] Energy of hydrogen bonded water dimer predicted by theory is -4.77 kcal/mol. [5] In this study, we performed an analysis of non-coordinated water containing structures archived in Cambridge Structural Database (CSD) as well as *ab-initio* calculations on a range of bond angles and bond lengths of water molecule and water dimers. We analyzed different geometrical parameters. The results of analysis of crystal structures showed that there is a large discrepancy of both the bond length and the bond angle values form the ideal ones. For example, the range of the bond angles of X-ray solved structures having R factor ≤ 0.05 is 22.43º-180.00º, while reliable bond angles predicted by calculations are in the range of ca. 93.2º-116.4º. Consequently, it would lead to at least 15% of X-ray solved structures that contain questionable water molecule geometries. Calculations on hydrogen bond potential energy surface were compared with the analysis of the all hydrogen bonds of non-coordinated water molecules in the CSD. We were able to correlate the calculated data with two regions of hydrogen bonded water dimers found in the CSD.

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