How flexible is the water molecule structure? Cambridge Structural Database and *ab initio* calculations study.

Milan R. Milovanović[1], Jelena M. Živković[1], Dragan B. Ninković[1], Ivana M. Stanković[2], Snežana D. Zarić[3,4]

[1]Innovation center of the Faculty of Chemistry, Studentski trg 12-16, Belgrade, 11000, Serbia; [2]Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia; [3]Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, 11000, Serbia; [4]Texas A&M University at Qatar, Education City, PO Box 23874, Doha, Qatar;

milovanovic@chem.bg.ac.rs

Water molecules are omnipresent in nature and are a key part of many life processes. Due its ability of hydrogen binding water molecule plays an important role in the packing of small molecule crystal structures. Over the past years, the structure of a water molecule has been intensively studied. [1] The experimental values for a free water molecule in the gas phase are the bond angle (H–O–H) of 104.52 ± 0.05° and the bond (O–H) length of 0.9572 ± 0.0003 Å. [2] Neutron diffraction experiments of liquid water showed that the bond angle increases to 106.1 ± 1.8° and the bond length increases to 0.970 ± 0.005 Å. [3] Most of the bond angles in structures of ice have values close to a tetrahedral angle. However, in some of the ice structures, the bond angles and bond lengths remarkably deviates. Calculations based on the spectroscopic potential energy surface showed the equilibrium structure of a water molecule with the bond angle of 104.501 ± 0.005° and the bond length of 0.95785 ± 0.00005 Å. [4] In this study, [5] 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. The results of the analysis of crystal structures solved by neutron as well as by X-ray diffraction analysis showed a large discrepancy of both the bond angle and bond length values. Namely, the ranges of the bond angle and the average bond lengths of neutron solved structures having R factor ≤ 0.05 are from 100.74° to 113.92° and from 0.91 Å to 0.99 Å respectively. The corresponding range of the bond angle of X-ray solved structures is from 13.27° to 180.00°. High level ab initio calculations predicted a possibility for energetically low-cost (±1 kcal mol–1) changes of both the bond angle and bond lengths in a wide range, from 96.4° to 112.8° (Fig. 1) and from 0.930 A to 0.989 A (Fig. 1), respectively. Consequently, it would lead to at least 15% of X-ray solved structures that contain questionable water molecule geometries.

Keywords: water molecule, bond angle, bond length, CSD, ab initio calculations