A systematic electronic structure study of the O?O bond dissociation energy of hydrogen peroxide and the electron affinity of the hydroxyl radical

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 Hydroxyl radical reduction and peroxide bond breaking in hydrogen peroxide are reactions involved in various processes such as the Fenton reaction, which has applications as e.g. groundwater remediation. Here, we study these two reactions from a thermodynamical point of view through the bond dissociation energy (BDE) of the O?O bond in hydrogen peroxide and the electron affinity (EA) of the hydroxyl radical. High-level ab-initio calculations at the complete basis set (CBS) limit were carried out, and the performance of different DFT-based methods was addressed by following a specific classification on the basis of the Jacob?s ladder in combination with various Pople?s basis sets. The ab-initio calculations at the CBS limit are in agreement with experimental reference data and identify a significant contribution of the electron correlation energy to the BDE and EA. The studied DFT-based methods were able to reproduce the ab-