Electron localization function and electron localizability indicator applied to study the bonding in the peroxynitrous acid HOONO.

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Streszczenie

The ground-state electronic structure of peroxynitrous acid (HOONO) and its singlet biradicaloid form (HO···ONO) have been studied using topological analysis of the electron localization function (ELF), together with the electron localizability indicator (ELI-D), at the DFT (B3LYP, M05, M052X, and M06), CCSD, and CASSCF levels. Three isomers of HOONO (cis-cis, cis-perp, and trans-perp) have been considered. The results show that from all functionals applied, only B3LYP yields the correct geometrical structure. The ELF and ELI-D-topology of the O-O and central N-O bonds strongly depends on the wave function used for analysis. Calculations carried out at CAS (14,12)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVTZ level reveal two bonds of the charge-shift type: a protocovalent N□O bond with a basin population of 0.82-1.08e, and a more electron depleted O-O bond with a population of 0.66-0.71e. The most favorable dissociation channel (HOONO → HO + ONO) corresponds to breaking of the most electron-deficient bond (O□O). In the case of cis- and trans-HO···ONO, the ELF, ELI-D, and electron density fields results demonstrate a closed-shell O···O interaction. The α-spin electrons are found mainly (0.64e) in the lone pairs of oxygen V(i) (= 1,2)(O) from the OH group. The β-spin electrons are delocalized over the ONO group, with the largest concentration (0.34e) on the lone pair of nitrogen V(N).

Adres publiczny

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