AB INITIO MOLECULAR ORBITAL CALCULATIONS ON $[O_2.(H_2O)_n]^+$ CLUSTER IONS

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As the first ionization energy of O_2 is 12.08 eV, O_2 is easily photoionized by solar radiation. As a result O_2^+ is a major constituent of the upper atmosphere, notably the E-region at altitude greater than 85 km. One of the issues of current interest in the chemistry of the upper atmosphere, concerns formation of the proton hydrates $H^+(H_2O)_n$ through the hydration of the O_2^+ ions. The proton hydrates mainly populate the D-region of the upper atmosphere below 82 km.

We calculate minimum energy isomers, vibrational frequencies, stepwise binding energies and thermodynamics parameters (ΔH°, ΔS°, and ΔG°) for the cluster ions $O_2^+.(H_2O)_n$, n=1-3 at a high ab initio level of theory. Relative electronic energies were calculated at RCCSD(t)/aug-cc-pVTZ//UMP2/6-311++G(3df,3pd) level. The inclusion of zero point energy (ZPE) and the full counterpoise correction for the basis set superposition error (BSSE) is essential to obtain the correct energy ordering for the different isomers of a cluster ion in different electronic states. The nature of stepwise hydration processes is discussed based on the isomeric structure obtained. A mechanistic pathway for the formation of proton hydrates from the $[O_2.(H_2O)_n]^+$ ions will be illustrated.

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