ELECTRONIC STRUCTURE STUDIES OF ELECTRON- AND X-RAY-IRRADIATED MOLECULES

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Abstract

This work applies various electronic structure methods to the electron- and X-ray-irradiated molecules. The goals of these computational studies range from calculating the physically inaccessible properties for analysis of experimental results to establishing accurate and computationally efficient methods facilitating understanding of experimental data.

Electronic structure methods that are used in this work are the density functional theory, Hartree-Fock, Møller–Plesset perturbation theory, and the coupled cluster technique.

Low-energy (70 eV) electron irradiation effects on the mixture of the nitrogen and methane gases in the complex chemistry of the Titan's atmosphere including cosmic rays and atmospheric lightning are studied computationally. The observed ionic species resulting from the electron irradiation, their chemical structures and binding energies are computed and analyzed with an emphasis on the heterogeneous structure formation, particularly on molecules containing CN bonds important in understanding the synthesis and nature of organic species' formation in Titan's atmosphere.

The process of monocarbon ionic cluster formation under low-energy electron irradiation in cold helium nanodroplets doped with nitrogen/methane mixtures is studied computationally. Electronic structure calculations determining the geometrical structures of these clusters and their binding energies enable the drawing of important conclusions on the conditions controlling the clusters formation.

Finally, a number of density functionals and Gaussian basis sets are benchmarked for calculation of the core electron binding energies for carbon, nitrogen, and oxygen nuclei in the first-row hydrides methane, ammonia, and water, and the multi-conformational amino acids – glycine, alanine, proline, threonine, and methionine. The goal is to establish methods having potential to aid analysis of experimental X-ray photoelectron spectra on compounds such as amino acids, DNA nucleosides, and large polypeptides in various environments. A number of promising density functionals, basis sets, and their unique combinations are identified that reproduce accurately the experimental results for the absolute binding energies and also for the intramolecular and intermolecular shifts.