Radiation induced damage in biomolecules. An *ab initio* molecular dynamics study on crystalline α-L-rhamnose

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In order to understand mechanisms of radiation damage to biomolecules, it is necessary to describe the primary radiation products in the smaller constituents of larger molecular complexes. Ionizing radiation induces mainly one-electron reduction- and oxidation products. These charged primary radicals interact with molecules in their environment, forming new, more stable and often electrically neutral radical species. The radical species are detected by EPR and related experimental techniques, and DFT simulations often accompany the experimental evidence in order to determine the radical structures with certainty.

As several radical species are formed upon irradiation, simple geometry optimizations are not able to access different minima of the potential energy surface using the same input. Modeling radiation products therefore normally require manual manipulation of the geometrical structures. This is often achieved by (re)moving hydrogen atoms or breaking bonds. When this approach does not render radical structures comparable to the experimental data at hand, the experimental data remain unexplained.

In this study the single crystal carbohydrate α-L-rhamnose was modeled by DFT calculations and application of periodic boundary conditions as a test case for a method which produces different radical species without the bias of the researcher. We have used *ab initio* MD simulations in order to study creation of radical species by ionization. This is achieved by starting from different input geometries on the potential energy surface and using different sets of (random) initial velocities normalized to either 100 K or 200 K. 160 MD simulations were produced where an electron was removed or added to the system. This resulted in the production of twelve different radical species of five different types, which all had do be assessed by calculation of hyperfine coupling tensors for comparison with experimental evidence. Out of these twelve, three were found to compare well with experimental data. All types of experimentally observed molecular radical species found in the literature on this system were produced in our study.