Elucidation of radiation-induced processes using DFT calculations

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Ionizing radiation usually induces different types of radicals in biomolecules. The selective formation of certain species that is often displayed leaves several questions regarding the radiation chemistry. By knowing which radicals are generated and via what kind of mechanism, ultimately a better understanding can be obtained of why radiation gives rise to a particular species. In view of the complexity of this problem, a good model system to examine such processes has to be simple and relevant, ideally resembling more interesting biomolecules, such as proteins or DNA strands.

Single crystals of basic amino acids – e.g. alanine – have since long served as model systems and are even directly applicable as dosimeters. Several studies have concentrated on the nature and formation mechanism of the radiation-induced radicals in these crystals using electron paramagnetic resonance (EPR) spectroscopy [1]. Although there is a general consensus of which species are formed, details with regard to the precise mechanism are still lacking. In particular, the interaction of the radical with its molecular environment is still largely unknown. Furthermore, the associated dynamic processes are not fully understood [2].

In this work, density functional theory (DFT) is used to follow the reaction profile of radiation damage in solid-state the amino acid alanine on a step-by-step basis. Possible routes are explored and their probability is assessed on the basis of energetic considerations. The identity of each stable radical or intermediate is corroborated by comparing calculated EPR properties with measurements, if available [3]. Ab initio calculations are performed using the CP2K software package, in which the molecular environment of the radical is appropriately taken into account by applying periodic boundary conditions on the alanine crystal structure.

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