

Which role do excited states play in radiation damage to organic solid-state compounds?

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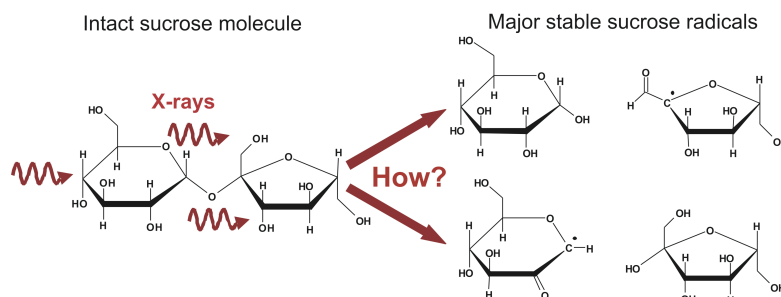
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Ionizing radiation induces radicals in organic materials. When such species are created in biological macromolecules like DNA, they harm living organisms. This detrimental effect is explicitly exploited for the sterilisation of e.g. foodstuffs, and radiation-induced radicals are quantitatively used for radiation dosimetry purposes. For understanding radiation actions at different levels of molecular and cellular organisation, knowledge of the radical structures and their formation mechanisms is of fundamental importance. In this context, radiation-induced processes in solid sugars are studied, among others, to gain insight into the role of the deoxyribose unit in the radiation chemistry of DNA.

X-irradiation typically gives rise to a variety of primary radicals in these systems, which transform into stable radicals or diamagnetic species via one or more radical reactions. By combining electron magnetic resonance experiments and density functional theory (DFT) calculations, we recently identified the major stable [1,2], as well as the major primary [3] radiation-induced radicals in solid *sucrose* (see figure). We are currently investigating how the primary radicals transform into the stable ones.

A general but important observation is that in sucrose and similar carbohydrates, e.g. rhamnose, the primary radical formation (typically by way of net H-abstraction) is selective: it preferentially takes place at particular carbons and oxygens. This selectivity apparently cannot be explained simply on thermodynamical grounds. It may be hypothesised that, after the initial oxidation event (leaving the radical cation in an excited state), the hole ‘migrates’ to a particular carbon or oxygen, after which de-excitation and deprotonation processes yield a neutral radical. It is our goal to examine factors possibly explaining the experimentally observed selectivity. So far we have made some preliminary ground-state calculations on energy profiles of deprotonation reactions in rhamnose single crystals, as well as time-dependent DFT calculations of excited states in this system.



References [1] H. De Cooman, E. Pauwels, H. Vrielinck, E. Sagstuen, F. Callens and M. Waroquier, *J. Phys. Chem. B*, **112**, 7298 (2008); [2] H. De Cooman, E. Pauwels, H. Vrielinck, E. Sagstuen, S. Van Doorslaer, F. Callens and M. Waroquier, *Phys. Chem. Chem. Phys.*, **11**, 1105 (2009); [3] H. De Cooman, E. Pauwels, H. Vrielinck, E. Sagstuen, M. Waroquier and F. Callens, *J. Phys. Chem. B*, **114**, 666 (2010).