

# Computational Study of a Fourth Stable Radical in X-irradiated Sucrose

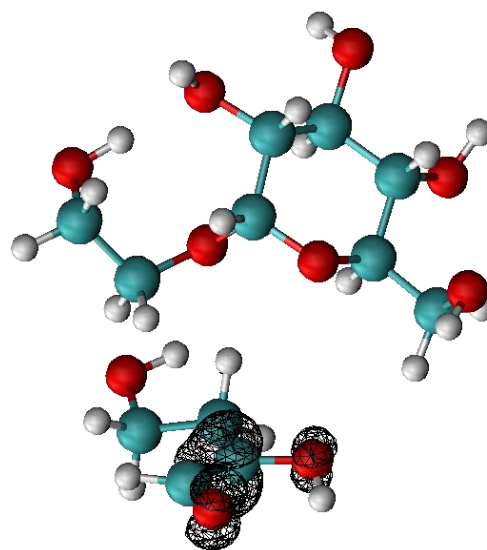
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Ionizing radiation produces radicals in solids, which are often well suited for studies by electron paramagnetic resonance (EPR) spectroscopy. Radiation-induced radicals in sugars are particularly interesting as model systems for sugar-containing macromolecules. Thorough characterization of radicals enables their identification and understanding of their chemical reaction pathways. This knowledge may subsequently provide insight into the radiation chemistry of more complex sugar-containing and biologically relevant systems, e.g. DNA and RNA.

Sucrose, also known as the main component of table sugar, presents a practical interest as a versatile dosimetric system. The stable radiation-induced EPR spectrum of sucrose has a sufficiently low detection limit and a considerable linear dose response range, which makes it a viable candidate for emergency dosimetry and characterization of radiation-sterilized foodstuffs. The multicomponent nature of the spectrum has slowed down further improvement of dose assessment protocols, which in turn motivated a series of investigations to address this issue.

Recently, it was shown that four radical species are sufficient to completely explain the dosimetric spectrum of X-irradiated sucrose. Three radicals have been identified prior to this by combining electron-nuclear double resonance spectroscopy with density functional theory (DFT) calculations [1, 2]. A similar approach has been applied to the fourth species, yielding its chemical structure [3]. The exact location of the radical in the crystal still remains unknown. In this contribution, we present results of our efforts to identify this last known stable species using periodic DFT calculations. The model we propose (Fig. 1) involves abstractions of H and O atoms, and scission of multiple bonds in the fructose unit. This effectively breaks the sucrose molecule into two parts, creating a detached radical molecule, suspended by hydrogen bonds.



*Figure 1. Optimized structure and spin density plot of a possible model of the fourth stable radical species in irradiated sucrose.*

1. De Cooman, H., Pauwels, E., Vrielinck, H., Dimitrova, A., Yordanov, N., Sagstuen, E., Waroquier, M. and Callens, F. *Spectrochim. Acta A*, 2008, 69, 1372–1383.
2. De Cooman, H., Pauwels, E., Vrielinck, H., Sagstuen, E., Callens, F., and Waroquier, M. J. *Phys. Chem. B*, 2008, 112, 7298–7307.
3. Kusakovskij, J., Caretti, I., Van Doorslaer, I., Callens, F., and Vrielinck H. *PCCP* (accepted for publication), 2016.