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Research paper

On the identity of the last known stable radical in X-irradiated sucrose

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ABSTRACT

Identification of radiation-induced radicals in relatively simple molecules is a prerequisite for the understanding of reaction pathways of the radiation chemistry of complex systems. Sucrose presents an additional practical interest as a versatile radiation dosimetric system. In this work, we present a periodic density functional theory study aimed to identify the fourth stable radical species in this carbohydrate. The proposed model is a fragment suspended in the lattice by hydrogen bonds with an unpaired electron at the original C5' carbon of the fructose unit. It requires a double scission of the ring accompanied by substantial chemical and geometric reorganization.

1. Introduction

Sucrose ($C_{12}H_{22}O_{11}$) can be found in almost every household as the main constituent of table sugar, as a sweetener in foodstuffs or as a component of medication [1]. Accidental or intentional exposure of this disaccharide to ionizing radiation leads to formation of free radicals. Knowledge of the radical composition permits mapping of chemical reaction pathways, which may be of interest for future drug design and food processing techniques. Studies of the radical catalysis of biomass sugars are also likely to benefit from this knowledge [2–4]. In its pure form, sucrose is considered to be an interesting solid state electron paramagnetic resonance (EPR) dosimetric system with a broad range of potential applications [5–7]. Despite all of the advantages of sucrose, like a considerable linear dose response and a relatively low detection limit, the multicomponent nature of its radiation-induced EPR spectrum has slowed down further improvement of dose assessment protocols. A complete understanding of the spectrum may improve this situation.

For the aforementioned reasons, considerable effort has been devoted to identifying stable and unstable radicals in irradiated sucrose using EPR spectroscopy data. The stable spectrum of irradiated sucrose has been known for almost sixty years [8], but systematic studies directed at determining chemical structures were started only in the late eighties [9]. In the course of the last decade, the presence of four different species was established. All of them were thoroughly characterized using electron-nuclear double resonance spectroscopy (ENDOR) and three out of four were convincingly identified by comparing experimental **g** and hyperfine coupling (HF) tensors with density functional theory (DFT) calculations [10–13]. For convenience, chemical structures of these radicals are presented in Fig. 1 together with a pristine sucrose molecule and the labeling scheme. In all previous studies, ENDOR characterization was performed at 110 K several days after room temperature (RT) irradiation. (For a thorough discussion of the topic, the reader is referred to Ref. [14].) In the present contribution, we propose and validate a model for the last unidentified stable radical species. It is demonstrated that the unpaired electron density is centered close to the pristine C5' site in the fructose unit and implies rather intricate rearrangements of the host molecule, resulting in an isolated radical fragment, suspended by hydrogen bonds in the lattice. Calculations based on the proposed model fit the experimental data remarkably well, which strongly suggests that the model is correct. This completes our understanding of the dominant stable radical structures formed in crystalline sucrose by X-irradiation.

2. Computational methods

Periodic DFT calculations were employed to test radical models, devised from the experimental data [13] and solid-state radiation chemistry principles. The calculation methodology has been developed and validated in other studies on various carbohydrates and amino acids [14–16]. The model validation procedures rely on a comparison of experimental **g** and HF tensors to calculated ones. For a given pair of tensors, agreement is considered very good if deviation angles between their principal directions are of the order

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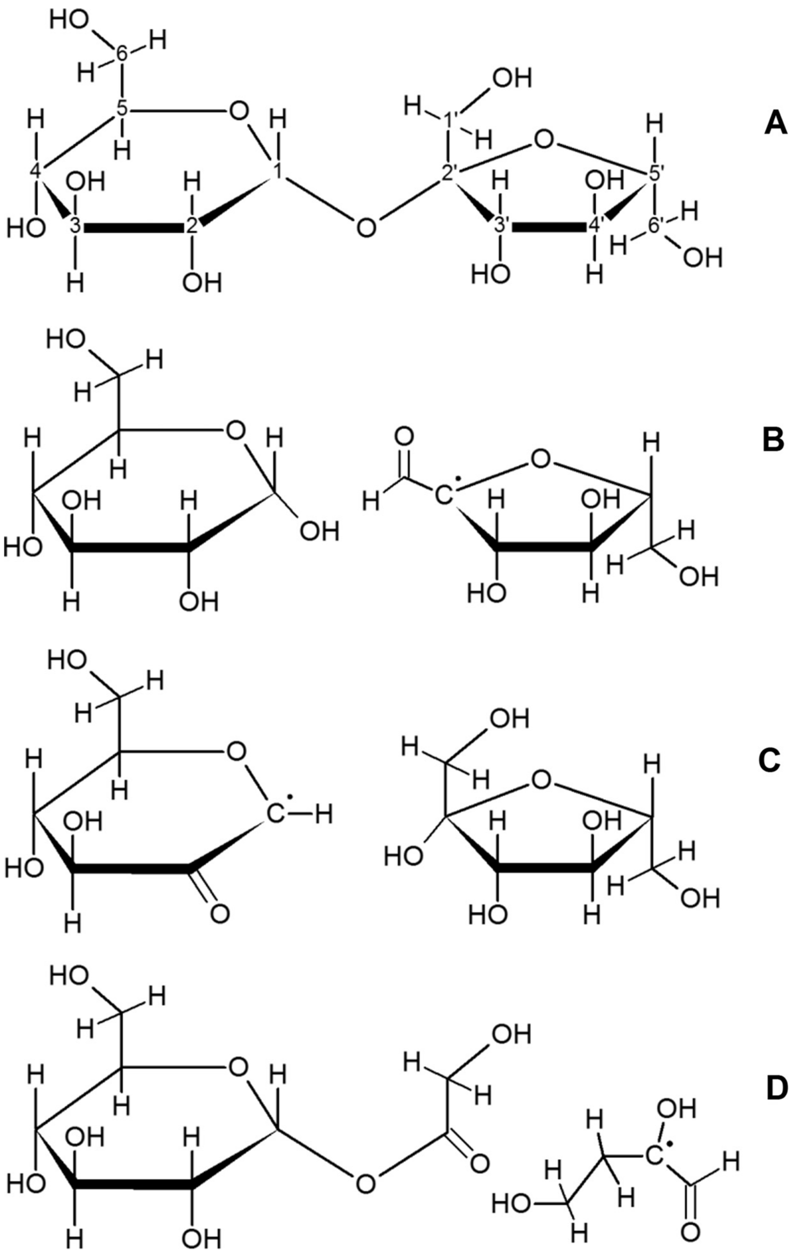

Fig. 1. Chemical structures of a pristine sucrose molecule (A), known stable radical species (B — T1, C — T2/T3) and the proposed model for the fourth as yet unknown species (D). Throughout this work, carbon atoms are numbered as shown in panel A: hydrogen and oxygen atoms are labeled according to the carbon to which they are bound, with the exception of hydroxyl hydrogen atoms, which are numbered according to the oxygen to which they are bound. The glycosidic, the glucose and the fructose ring oxygen atoms are labeled as O1, O5 and O5', respectively.

of 10° or less, the anisotropy of principal values is reproduced and the isotropic parts coincide within an accuracy of about 15%. In principle such agreement could be further improved for specific systems by fine tuning the level of theory, i.e. the basis set and the functional, but this would trade off the generality of the approach.

The crystal structure of sucrose is monoclinic with space group $P2_1$. This implies two molecules in a unit cell related by a twofold screw axis ($\langle b \rangle$). All tensors are presented for the same symmetry site, which was chosen to assure the smallest deviation angles for the largest HF couplings. The lattice parameters were assumed to be as determined by Brown and Levy [17] in a neutron diffraction analysis: $a = 1.0868$ nm, $b = 0.8710$ nm, $c = 0.7761$ nm and $\beta = 102.97°$, where β denotes the angle between $\langle a \rangle$ and $\langle c \rangle$ axes. The $\langle a^*bc \rangle$ orthogonal reference frame was chosen in accordance with previous work, where $\langle a^* \rangle$ is perpendicular to $\langle b \rangle$ and $\langle c \rangle$. The chemical structure of the sucrose molecule and the labeling scheme are both shown in Fig. 1A.

Calculations were performed using the CP2K software package [18] and the BLYP exchange–correlation functional [19,20]. To prevent interactions of the radical with its periodic images, a supercell doubled in the $\langle c \rangle$ crystallographic direction ($\langle ab2c \rangle$) was used. Geometries were first optimized using the Gaussian and plane waves (GPW) dual basis set method [21] with a plane wave cutoff energy of 300 Ry, TZV2P GTH Gaussian basis sets [22] and GTH pseudopotentials [23,24]. Then the obtained geometries were further refined on a higher level of theory: all-electron Gaussian and augmented plane waves (GAPW) [25] with an energy cutoff of 350 Ry and 6-311G** Gaussian basis sets [22,26]. The HF tensors were calculated as described in Ref. [27] using the same level of