

# **Structural specificity of alkoxy radical formation in crystalline carbohydrates**

## **SUPPLEMENTARY INFORMATION**

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### Comparison of calculated and measured EPR properties for the stable alkoxy radicals

In line with previous studies<sup>1</sup>, only the calculated EPR properties of the O4-centered alkoxy radical can be matched to the experimental magnetic resonance data<sup>2</sup>. This, again, confirms that it is not the O1- and O2-centered species that are observed in irradiated rhamnose crystals but only the O4 alkoxy radical.

A comparison of calculated g-tensors with their experimental counterparts is shown in Table 1. The overall symmetry and magnitude of the g-tensor matches excellently with the measured g-tensor and calculated and measured eigenvector directions deviate by only a few degrees.

For the hyperfine couplings of the O4-centered radical (see Table 2), the differences between the calculated and measured properties are somewhat larger, but the agreement is nevertheless convincing. Some corrections to the experimental data as suggested by Pauwels *et al.*<sup>1</sup> have been applied here as well. All hyperfine couplings reported by Budzinski and Box<sup>2</sup> for the O4• radical were reproduced in the present computations, although couplings are not all assigned to the same atoms to which they were assigned by Budzinski and Box.

The overall agreement between theory and experiment is very good, apart from two inconsistencies: the magnitude of the H4 isotropic coupling is only about 40% of the experimental value, and two of the H2 eigenvector directions differ more than 20° from their experimental counterparts. The hyperfine coupling tensors of alkoxy radicals are however difficult to calculate accurately and very susceptible to even minute differences in the spin density distribution.

**Table 1:** Results from g-tensor calculations of the three stable radical structures compared to experimental values for the O4-centered alkoxy radical given by Budzinski and Box<sup>2</sup>. a\* refers to the orthogonal projection of the *a*-axis.

Radical	Principal values		Principal directions			Angular deviation from experiment /degrees
	g-tensor		a*	b	c	
O1•	2.0234		0.800	-0.304	0.517	54
	2.0094		0.360	0.932	-0.008	64
	1.9923		0.480	-0.193	-0.856	55
O2•	2.0267		0.835	-0.546	0.069	50
	2.0098		0.050	0.200	0.978	56
	2.0032		0.548	0.813	-0.195	29
O4•	2.0211		0.780	0.223	0.584	4
	2.0084		0.554	-0.679	-0.481	3
	2.0035		0.289	0.697	-0.653	4
Experimental data for the O4 radical	2.0202		0.759	0.198	0.619	
	2.0068		0.554	-0.694	-0.458	
	2.0018		0.339	0.691	-0.637	

**Table 2:** Computed hyperfine couplings (in MHz) for the O4 centered radical compared to experimental data (tensors A1 – A7, A1, A3 and A4 being exchangeable (ex)) given by Budzinski and Box<sup>2</sup>. See Fig. 1 for the atomic numbering scheme. Hw refers to a proton on the crystal water molecule that is hydrogen bound to O4 but not partaking in the deprotonation process. a\* refers to the orthogonal projection of the *a*-axis.

Theoretical values						Experimental data			
	A <sub>iso</sub>	A <sub>aniso</sub>	Principal directions			Angular deviation from theor. data /degrees	A <sub>aniso</sub>	A <sub>iso</sub>	
			a*	b	c				
H2	79.8	5.8	-0.246	-0.881	0.405	27	4.3	67.22	A5 <sup>2</sup>
		-1.7	0.489	0.248	0.836	28	-0.22		
		-4.1	-0.837	0.404	0.370	9	-4.04		
H3	5.7	9.4	0.590	-0.776	0.222	2	12.88	5.22	A2 <sup>2</sup>
		-1.1	-0.795	-0.606	-0.006	3	-0.19		
		-8.3	-0.139	0.173	0.975	0.4	-12.68		
H4	21.6	9.1	0.869	-0.480	0.124	4	9.70	53.90	A6 <sup>2</sup>
		-3.0	-0.412	-0.561	0.718	3	-1.97		
		-6.0	0.275	0.675	0.685	4	-7.72		
H6	4.9	2.4	-0.324	0.131	0.937	6	2.58	3.88	A7
		-0.5	0.641	0.759	0.116	6	-0.67		
		-1.9	-0.696	0.638	-0.330	4	-1.90		
HO3	-6.7	10.7	-0.464	0.068	-0.883	13	7.83	-5.20	A4 <sup>1,2</sup>
		-1.7	-0.631	-0.725	0.276	11	0.08		(ex)
		-9.0	-0.622	0.685	0.379	10	-7.93		
HO4	-2.7	15.5	-0.077	0.992	0.103	6	15.10	-3.02	A1
		-7.4	0.689	0.128	-0.714		-7.33		(ex)
		-8.1	0.721	-0.016	0.693		-7.73		
HW	-0.5	9.6	0.908	-0.412	0.079	4	10.82	0.05	A3
		-4.3	-0.364	-0.682	0.634		-4.89		(ex)
		-5.3	0.208	0.605	0.769		-5.92		

<sup>1</sup>Sign of the experimental tensor has been inverted.

<sup>2</sup>Experimental tensor has been changed in accordance with Pauwels *et al.*<sup>1</sup>.

## References:

1. E. Pauwels, R. Declerck, V. Van Speybroeck and M. Waroquier, *Radiat. Res.*, 2008, **169**, 8-18.
2. E. E. Budzinski and H. C. Box, *J. Chem. Phys.*, 1985, **82**, 3487-3490.