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Supporting Information

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The Benzylperoxyl Radical as a Source of Hydroxyl and Phenyl Radicals

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Supporting Information

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I. Synthesis and Matrix Isolation of the Benzylperoxy Radical 2

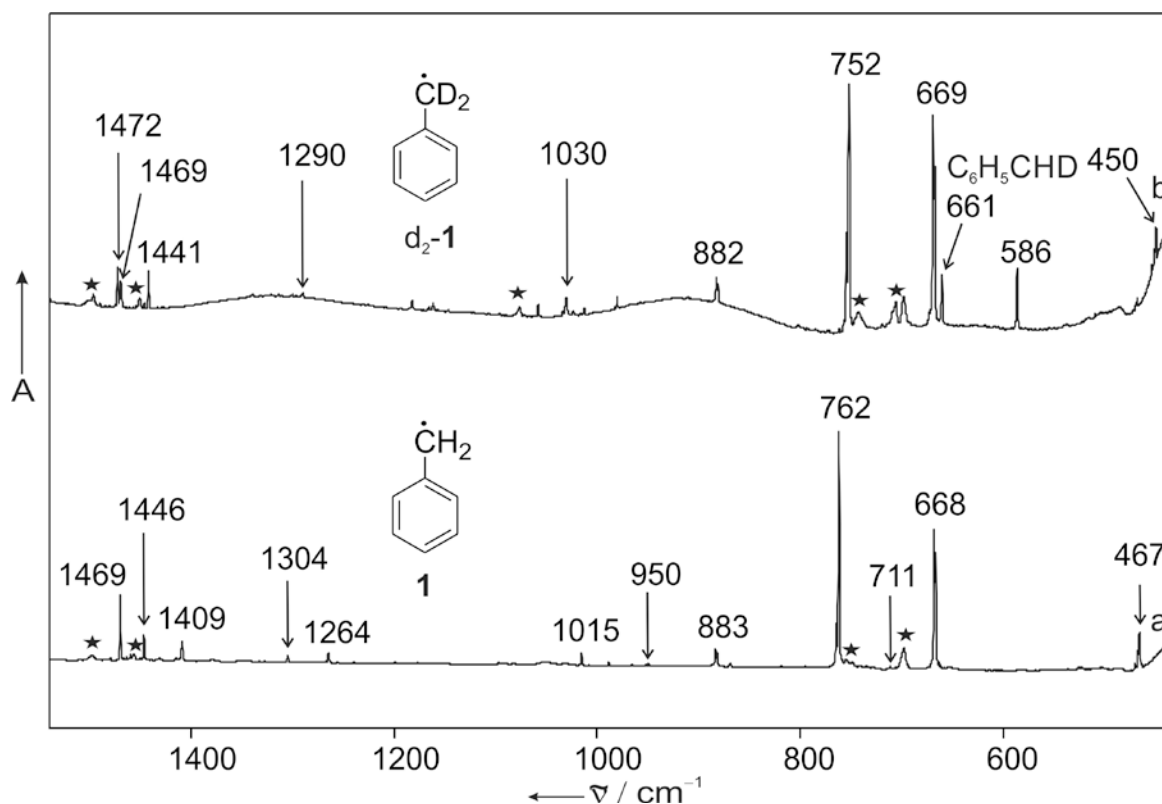


Figure S1. IR spectra showing the generation of radical **1** and d_2 -**1** in argon. (a) IR spectrum obtained after trapping the FVP products of **3** in argon at 3 K. (b) IR spectrum obtained after trapping the FVP products of d_4 -**3** in argon at 3 K. Peaks marked with (*) belong to the precursors **3** and d_4 -**3**, respectively.

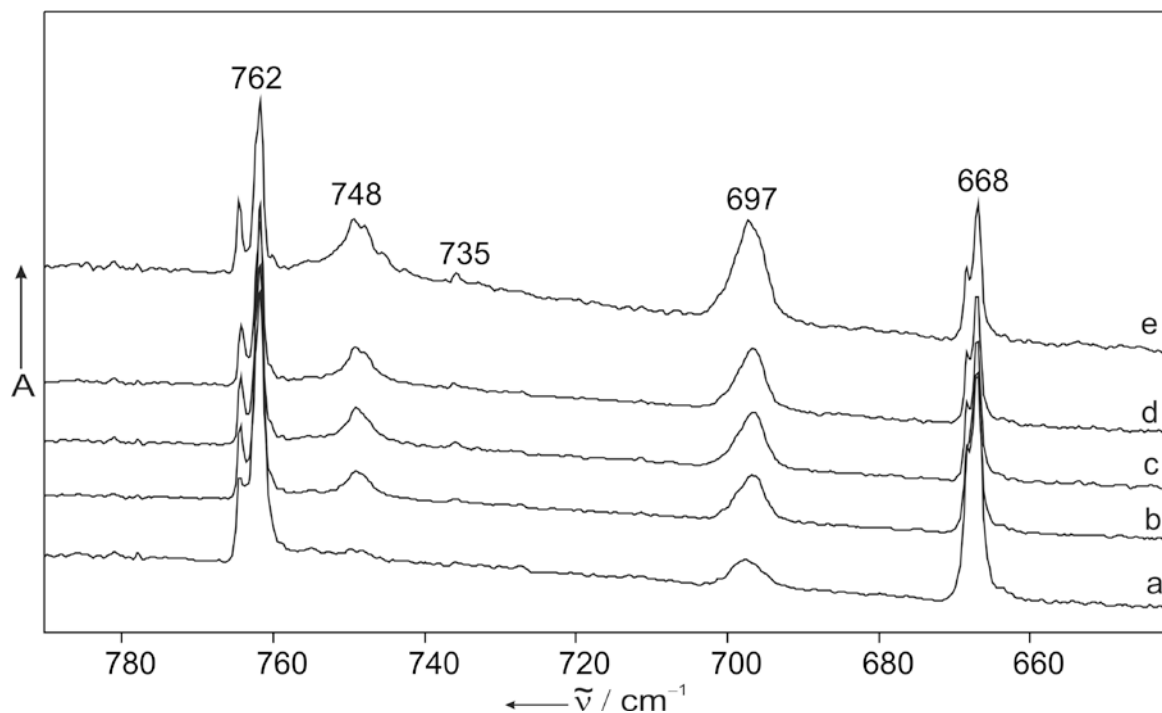


Figure S2. Annealing of the benzyl radical **1** in a 0.5% O_2 -doped argon matrix at 3 K. (a) IR spectrum obtained after trapping the FVP products of **3** in a 0.5% O_2 -doped argon matrix at 3 K. (b)-(d) Annealing of matrix (a) at temperatures of 20, 25, and 30 K, respectively. (e) Spectrum after annealing up to 30 K followed by cooling down to 3 K.

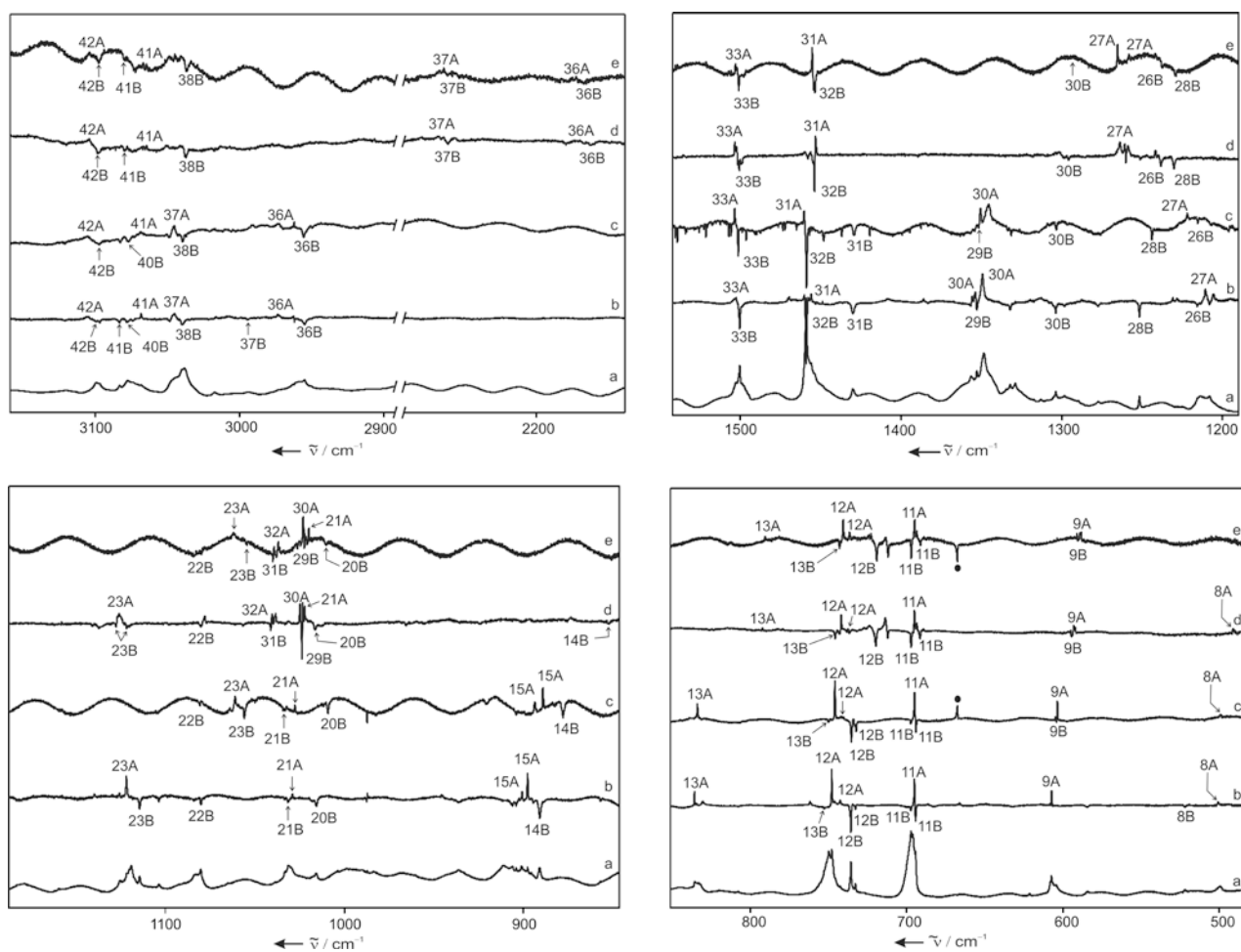


Figure S3. a) IR spectrum obtained after FVP of **3** at 620 °C and trapping the products in argon at 25 K. The spectrum was recorded after cooling to 3 K and shows bands assigned to **2**. b) – e) Difference IR spectra of four isotopomers of **2** showing changes induced by cooling the matrix from 25 K to 3 K. The first spectrum was taken immediately after cooling to 3 K, the second spectrum after a waiting time of approximately 15 min. Bands pointing downwards are decreasing in intensity, bands pointing upwards are increasing in intensity at 3 K. b) $2\text{-h}_2^{16}\text{O}_2$ c) $2\text{-h}_2^{18}\text{O}_2$ d) $2\text{-d}_2^{16}\text{O}_2$ e) $2\text{-d}_2^{18}\text{O}_2$. Bands labelled A are assigned to the major conformer **2a**, bands labelled B to the minor conformer **2b**.

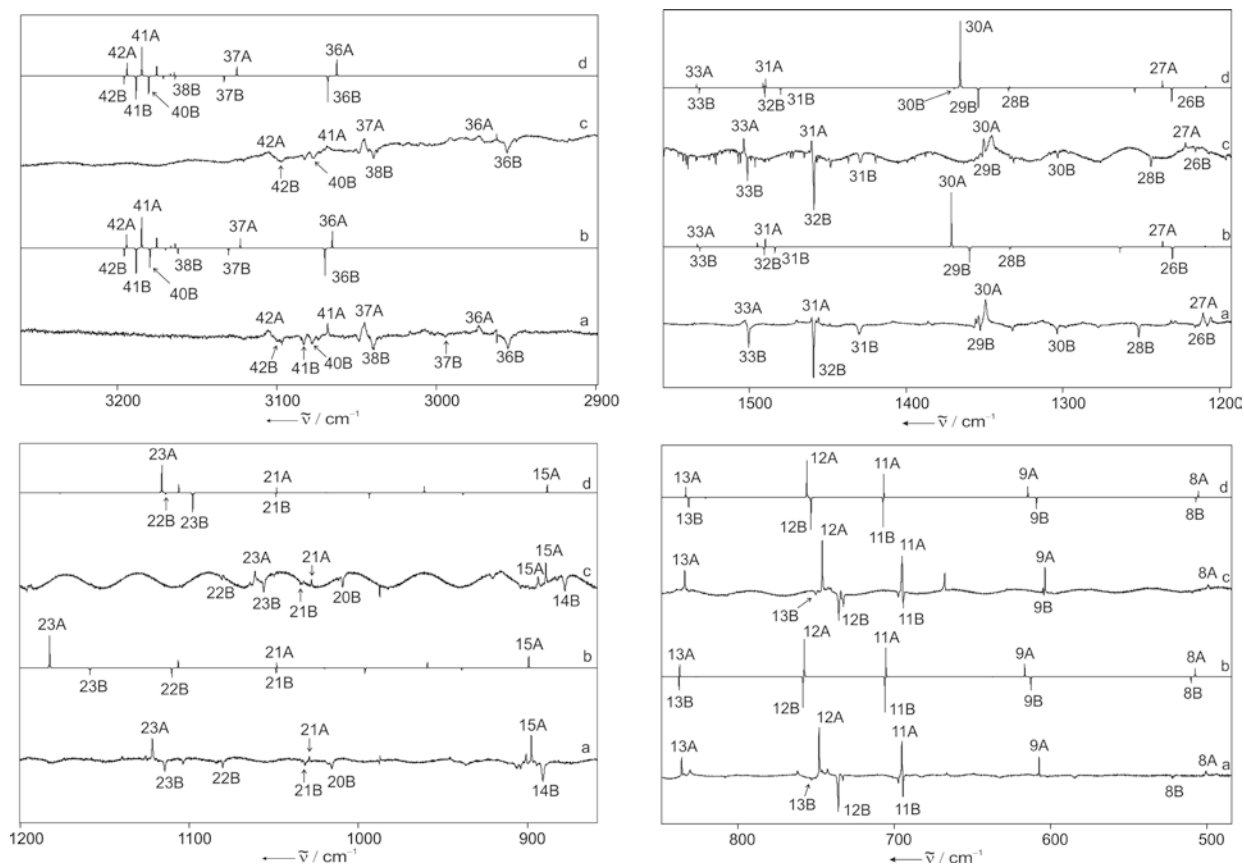


Figure S4. Difference IR spectra showing the interconversion of the two conformers of benzylperoxy radical (**2**) at 3 K. Bands pointing upwards are increasing in intensity, bands pointing downwards are decreasing in intensity. Difference IR spectra showing changes of (a) $2\text{-h}_2^{16}\text{O}_2$ and (c) $2\text{-h}_2^{18}\text{O}_2$ after keeping the matrix for several minutes at 3 K. Computed difference IR spectrum [B3LYP-D/6-311++G(2d,2p)] obtained by subtracting **2-gauche** from **2-anti** for: (b) $2\text{-h}_2^{16}\text{O}_2$ (d) $2\text{-h}_2^{18}\text{O}_2$. Bands labelled A are assigned to the major conformer **2a** (experimental spectra) or to **2-anti** (calculated spectra), bands labelled B to the minor conformer **2b** (experimental spectra) or to **2-gauche** (calculated spectra).

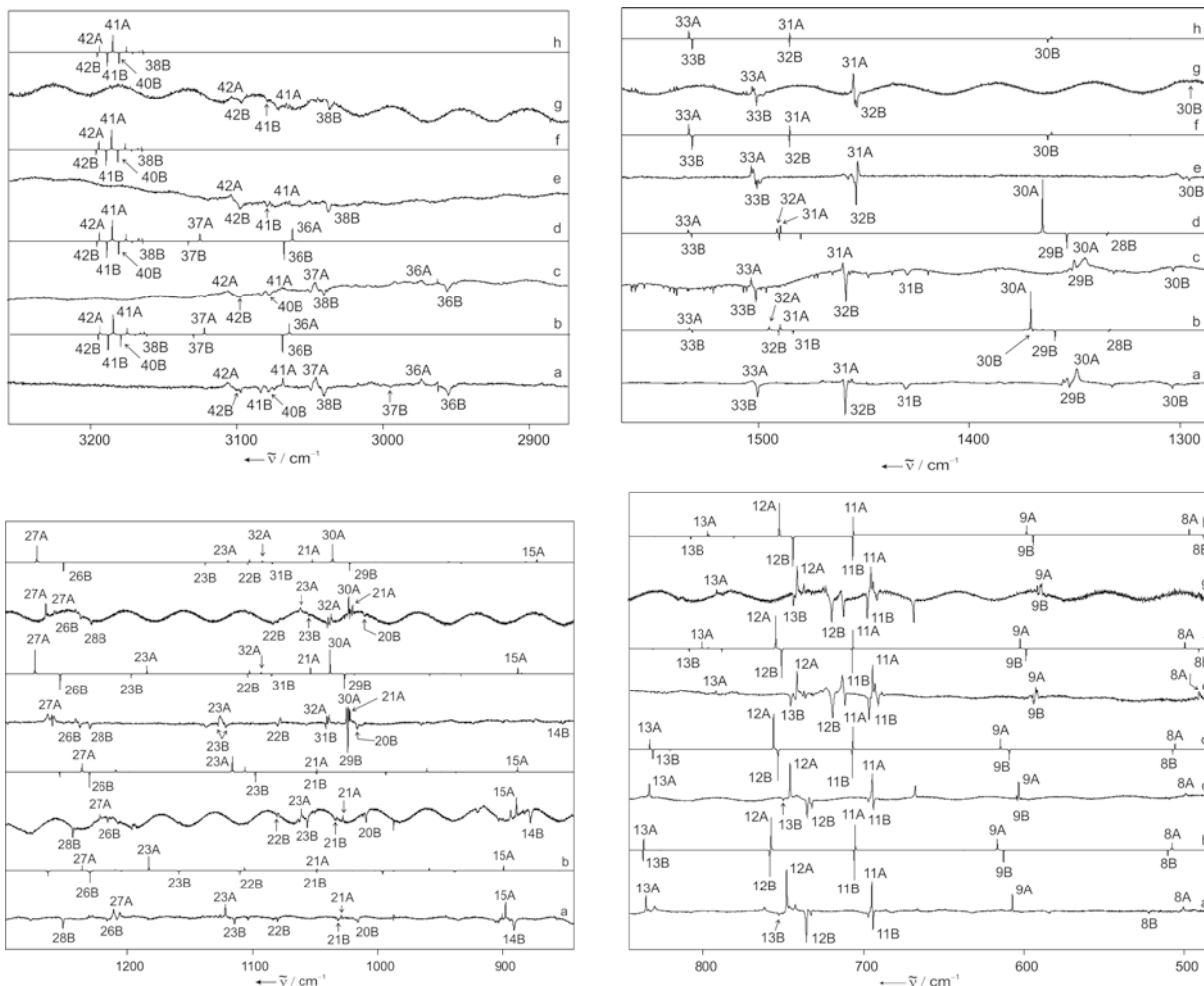


Figure S5. Difference IR spectra showing the interconversion of the two conformers of benzylperoxy radical (**2**) at 3 K. Bands pointing upwards are increasing in intensity, and bands pointing downwards are decreasing in intensity. Difference IR spectra showing changes of (a) **2**- $\text{h}_2^{16}\text{O}_2$, (c) **2**- $\text{h}_2^{18}\text{O}_2$, (e) **2**- $\text{d}_2^{16}\text{O}_2$, and (g) **2**- $\text{d}_2^{18}\text{O}_2$ after keeping the matrix for several minutes at 3 K. Computed difference IR spectrum [B3LYP-D/6-311++G(2d,2p)] obtained by subtracting **2**-gauche from **2**-anti for: (b) **2**- $\text{h}_2^{16}\text{O}_2$ (d) **2**- $\text{h}_2^{18}\text{O}_2$ (f) **2**- $\text{d}_2^{16}\text{O}_2$ (h) **2**- $\text{d}_2^{18}\text{O}_2$. Bands labelled A are assigned to the major conformer **2a** (experimental spectra) or to **2**-anti (calculated spectra), bands labelled B to the minor conformer **2b** (experimental spectra) or to **2**-gauche (calculated spectra).

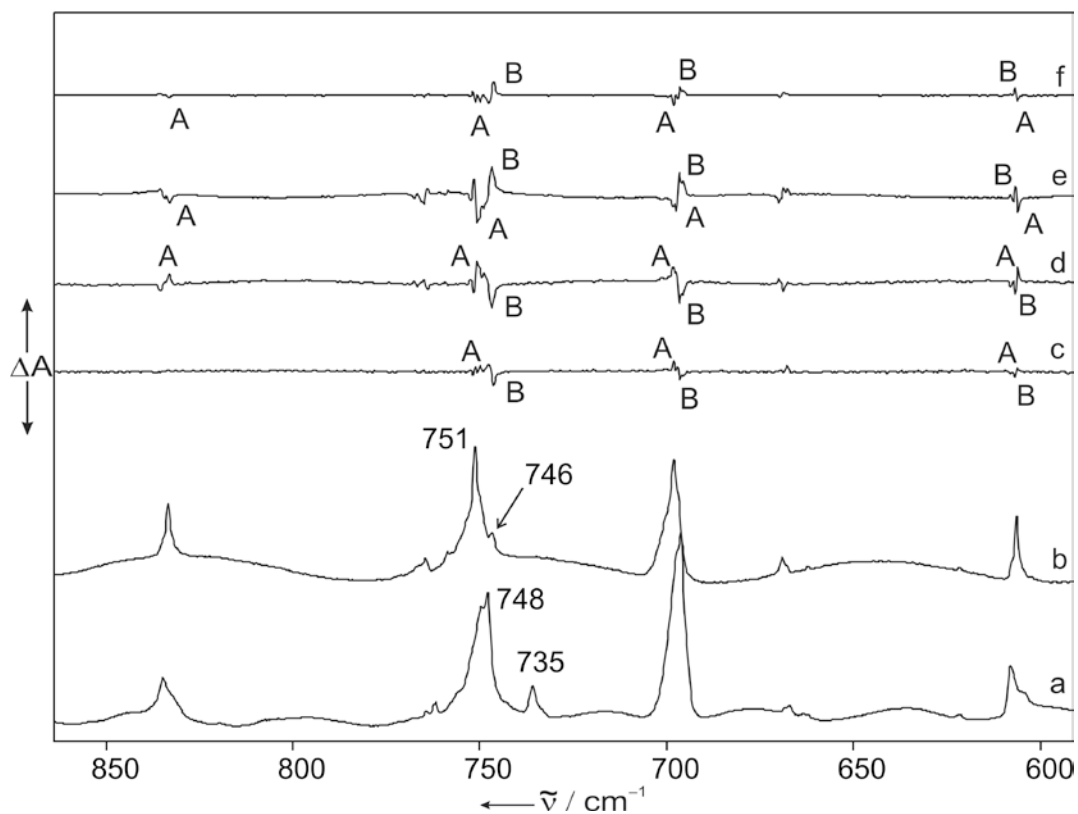


Figure S6. Difference IR spectra showing the interconversion of the two conformers of the benzylperoxy radical **2** at various temperatures. Bands pointing upwards are increasing in intensity and bands pointing downwards are decreasing in intensity. (a) Deposition spectrum of $2\text{-h}_2^{16}\text{O}_2$ at 3 K in argon. (b) Deposition spectrum of $2\text{-h}_2^{16}\text{O}_2$ at 3 K in nitrogen. (c) Difference spectrum obtained after annealing the matrix (b) at 10 K. (d) Difference spectrum after annealing the matrix (c) at 20 K. (e) Difference spectrum after cooling the matrix (d) at 10 K. (f) Difference spectrum obtained after cooling the matrix (e) at 3 K. Bands labelled A are assigned to the major conformer **2a**, bands labelled B to the minor conformer **2b**.

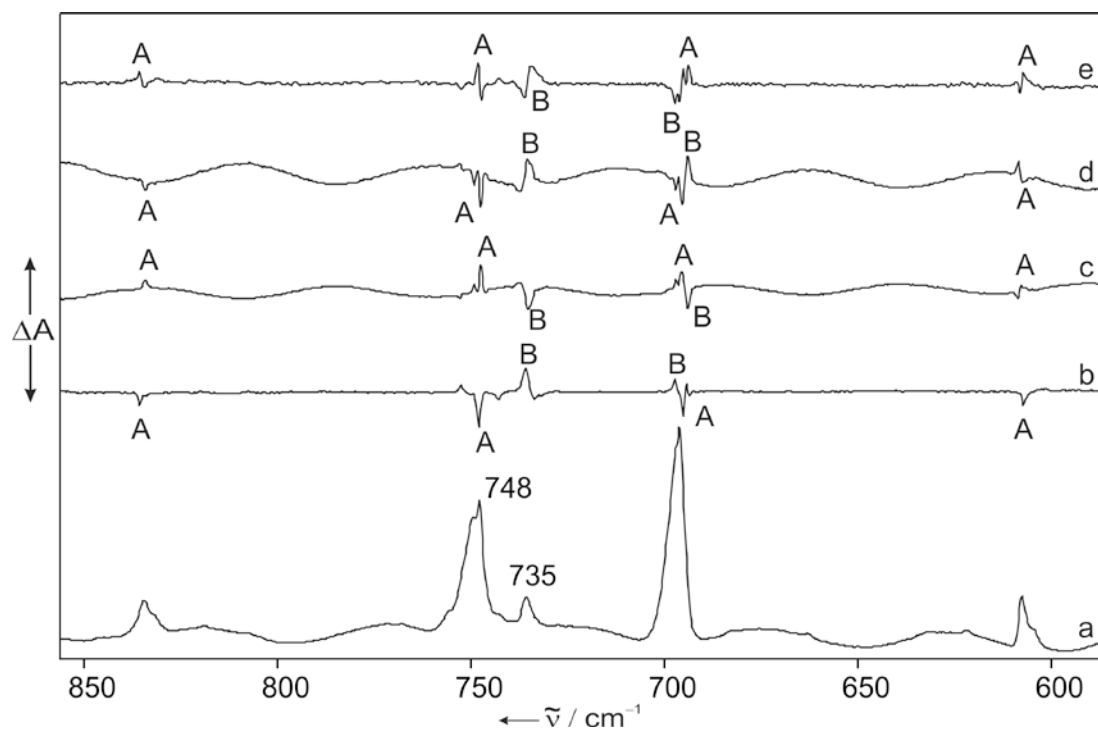


Figure S7. Difference IR spectra showing the interconversion of the two conformers of the benzylperoxy radical **2** at various temperatures. Bands pointing upwards are increasing in intensity and bands pointing downwards are decreasing in intensity. (a) Deposition spectrum of $2\text{-h}_2^{16}\text{O}_2$ at 3 K in argon. (b) Difference spectrum obtained after annealing the matrix (a) at 10 K. (c) Difference spectrum after annealing the matrix (b) at 25 K. (d) Difference spectrum after cooling the matrix (c) at 10 K. (e) Difference spectrum obtained after cooling the matrix (d) at 3 K. Bands labelled A are assigned to the major conformer **2a**, bands labelled B to the minor conformer **2b**.

II. Calculations [B3LYP-D/6-311++G(2d,2p)] on the Benzylperoxy Radical Conformers 2-anti and 2-gauche

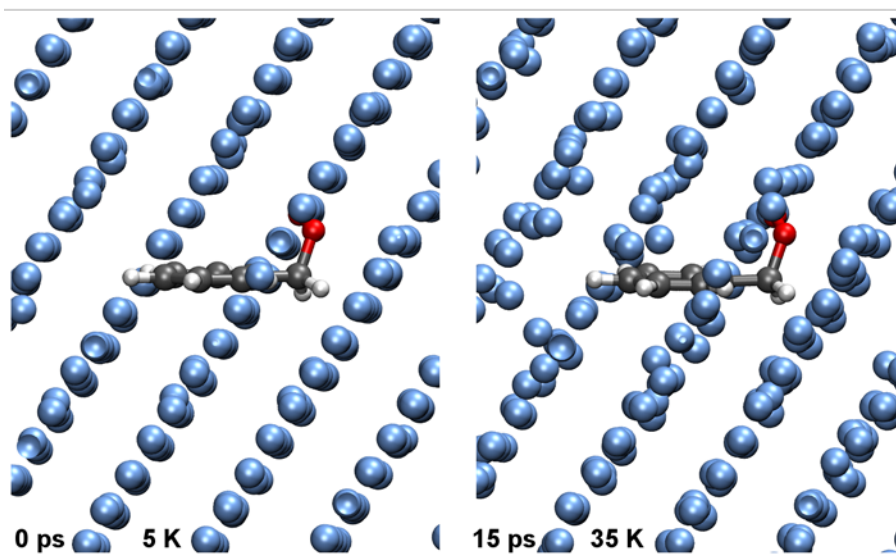
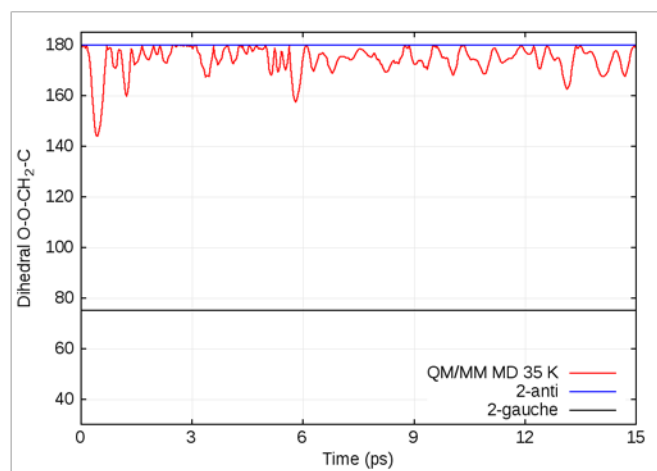


Figure S8. Top: Behavior of the dihedral angle that involved both oxygen atoms in **2** showing no interconversion between 2-anti and 2-gauche. Bottom: Snapshot of the QM/MM MD simulation showing the increasing disorder in the Ar matrix.

Table S1. Experimental and calculated [B3LYP-D/6-311++G(2d,2p)] IR vibrations (cm⁻¹) of conformer **2-gauche** and its different isotopomers

2-gauche B3LYP-D/6-311++G(2d,2p)																	
mode	H- ¹⁶ O				H- ¹⁸ O				D- ¹⁶ O				D- ¹⁸ O				assignments
	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^d Int _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^d Int _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^d Int _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^d Int _{Cal}	
8	522	8	510	8	-	-	507	7	-	-	491	6	-	-	488	6	C-CH ₂ str
9	608	5	613	18	604	12	609	17	594	26	599	18	590	12	594	18	CH/ CH ₂ oop
11	694	57	706	47	694	55	707	45	692	43	707	44	691	28	707	43	CH oop
	697	19	-	-	697	18	-	-	697	96	-	-	697	85	-	-	-
12	733	16	758	40	732	52	753	46	720	100	751	44	719	100	744	47	CH oop
	736	100	-	-	735	100	-	-	-	-	-	-	-	-	-	-	-
13	752	7	827	1	750	14	821	2	746	49	809	4	743	39	808	5	CC/C-CH ₂ str/ ring def
14	891	16	838	18	878	18	831	14	852	13	788	6	-	-	781	3	CH/CH ₂ /CO oop
20	1016	8	1020	0	1009	13	1019	0	1017	19	1019	0	1010	15	1018	2	-
21	1032	4	1049	2	1033	5	1049	2	-	-	1049	0	-	-	1048	1	CC str/ CH bend
22	1080	5	1110	4	1080	7	1114	0	1080	12	1104	4	1079	12	1104	4	CH bend
23	1115	10	1159	3	1056	15	1098	7	1122	13	1197	4	1054	12	1138	6	OO str
	-	-	-	-	-	-	-	-	1128	11	-	-	-	-	-	-	-
26	1216	2	1230	10	1215	7	1231	10	1238	16	1254	16	1238	17	1251	15	C-CH ₂ str
28	1251	11	1334	2	1243	14	1335	3	1230	22	1324	0	1229	15	1324	0	CC str./CH bend
30	1304	7	1370	2	1304	8	1369	1	1296	10	1363	1	1293	7	1363	1	CH bend
	1332	7	-	-	1331	8	-	-	-	-	-	-	-	-	-	-	-
29	1353	16	1360	13	1351	14	1354	14	1024	92	1026	15	1023	29	1022	13	CH ₂ wagging
31	1430	10	1484	5	1429	14	1480	5	1041	20	1085	2	1040	24	1085	2	CH ₂ scissoring
32	1459	59	1490	7	1458	74	1490	7	1454	65	1485	7	1454	42	1485	7	CC str/CH bend
33	1500	25	1531	4	1501	32	1532	4	1500	24	1532	4	1500	36	1532	4	CC str/CH bend
	-	-	-	-	-	-	-	-	1501	14	-	-	-	-	-	-	-
36	2955	6	3070	19	2955	10	3068	19	2168	6	2229	14	2173	4	2229	14	CH ₂ symm str
37	2994	3	3130	5	-	-	3133	5	2250	8	2331	4	2250	2	2331	4	CH ₂ asymm str
38	3039	5	3162	3	3039	5	3164	3	3037	12	3164	3	3037	8	3164	3	CH str
40	3078	3	3180	13	3077	3	3180	13	-	-	3180	13	-	-	3180	13	CH str
41	3083	4	3188	17	3082	4	3188	17	3080	7	3188	17	3080	5	3188	17	CH str
42	3097	4	3196	6	3097	4	3196	6	3097	10	3196	6	3097	7	3196	6	CH str

[a] Argon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the B3LYP-D/6-311++G(2d,2p) level of theory (unscaled). The assignment is based on band positions and intensities. [d] Calculated intensities in km/mol.

Table S2. Experimental and calculated [B3LYP-D/TZVPP//CHARMM] IR vibrations (cm⁻¹) of conformer **2-gauche** and its different isotopomers

2-gauche B3LYP-D/TZVPP//CHARMM													
Mode	H-O16			H-O18			D-O16			D-O18			assignments
	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	
8	522	8	517	-	-	511	-	-	493	-	-	490	C-CH ₂ str
9	608	5	612	604	12	607	594	26	598	590	12	594	CH/ CH ₂ oop
11	694	57	715	694	55	715	692	43	715	691	28	715	CH oop
	697	19	715	697	18	715	697	96	715	697	85	715	
12	733	16	765	732	52	759	720	100	755	719	100	748	CH oop
	736	100	765	735	100	759	-	-	755	-	-	748	
13	752	7	830	750	14	830	746	49	812	743	39	811	CC/C-CH ₂ str/ ring def
14	891	16	839	878	18	827	852	13	789	-	-	782	CH/CH ₂ /CO oop
20	1016	8	1020	1009	13	1020	1017	19	1020	1010	15	1019	-
21	1032	4	1046	1033	5	1046	-	-	1047	-	-	1046	CC str/ CH bend
22	1080	5	1104	1080	7	1096	1080	12	1098	1079	12	1098	CH bend
23	1115	10	1158	1056	15	1110	1122	13	1197	1054	12	1138	OO str
	-	-	1158	-	-	1110	1128	11	1197	-	-	1138	
26	1216	2	1230	1215	7	1230	1238	16	1253	1238	17	1251	-
28	1251	11	1338	1243	14	1338	1230	22	1327	1229	15	1327	CC str./CH bend
29	1304	7	1357	1304	8	1355	1296	10	1356	1293	7	1356	CH bend
	1332	7	1357	1331	8	1355	-	-	1356	-	-	1356	
30	1353	16	1364	1351	14	1361	1024	92	1030	1023	29	1027	CH ₂ wagging
31	1430	10	1474	1429	14	1474	1041	20	1080	1040	24	1079	CH ₂ scissoring
32	1459	59	1486	1458	74	1486	1454	65	1481	1454	42	1481	CC str./CH bend
33	1500	25	1529	1501	32	1529	1500	24	1528	1500	36	1528	CC str./CH bend
	-	-	1529	-	-	1529	1501	14	1528	-	-	1528	
36	2955	6	3058	2955	10	3058	2168	6	2222	2173	4	2222	CH ₂ symm str
37	2994	3	3126	-	-	3126	2250	8	2327	2250	2	2327	CH ₂ asymm str
38	3039	5	3159	3039	5	3159	3037	12	3159	3037	8	3159	CH str
40	3078	3	3177	3077	3	3177	-	-	3177	-	-	3177	CH str
41	3083	4	3187	3082	4	3187	3080	7	3187	3080	5	3187	CH str
42	3097	4	3199	3097	4	3199	3097	10	3199	3097	7	3199	CH str

[a] Argon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the M06-2X/6-311++G(2d,2p) level of theory (unscaled). The assignment is based on band positions and intensities.

Table S3. Experimental and calculated [B3LYP-D/6-311++G(2d,2p)] IR vibrations (cm^{-1}) of conformer **2-anti** and its different isotopomers

2-anti B3LYP-D/6-311++G(2d,2p)																	
mode	H-O16				H-O18				D-O16				D-O18				assignments
	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^d Int _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^d Int _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^d Int _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^d Int _{Cal}	
8	501	10	508	11	499	9	506	10	491	23	499	10	-	-	497	9	C-CH ₂ oop
9	607	40	617	16	603	53	615	16	593	38	602	15	589	46	598	14	CH/ CH ₂ oop
	608	5			605	9			595	11			591	33			
11	695	73	705	39	695	73	707	37	694	40	707	37	694	43	707	36	CH oop
	-	-			-	-			695	100			695	93			
12	742	11	757	49	742	7	756	53	738	12	754	48	737	38	752	52	CH oop
	748	100			746	100			742	80			741	100			
13	831	10	837	17	-	-	833	15	-	-	801	10	-	-	797	9	CC/ C-CH ₂ str Ring def
	836	36			834	38			792	14			790	18			
15	897	19	899	5	889	13	888	3	-	-	888	7	-	-	873	4	CH/CO oop
	900	7			894	7			-	-			-	-			
21	1029	4	1048	2	1028	6	1048	2	1022	34	1053	6	1020	32	1052	4	CH bend
23	1122	14	1183	12	1061	9	1116	10	1126	21	1184	8	1062	17	1120	4	OO str
27	1206	5	1236	5	1222	5	1237	5	1259	15	1274	24	1258	13	1272	26	C-CH ₂ str
	1211	9			-	-			1264	21			1266	53			
30	1350	23	1371	47	1346	18	1365	49	1023	42	1038	24	1022	27	1036	28	CH ₂ wagging
	1354	9			1351	14			1024	40			1023	69			
32	-	-	1495	4	-	-	1491	4	1025	-	1039	22	1037	33	1092	2	-
	-	-			-	-			1040	20			1039	25			
31	1456	6	1490	7	1460	10	1490	7	1453	28	1485	7	1455	57	1485	7	CC str./CH bend
	1460	6			-	-			-	-			-	-			
33	1503	4	1533	3	1503	12	1534	3	1503	14	1533	3	1502	19	1533	3	CC str./CH bend
	-	-			-	-			1504	21			1503	26			
36	2973	3	3065	12	2973	3	3062	12	2177	4	2225	10	2177	8	2225	10	CH ₂ symm str
37	3046	5	3123	7	3046	7	3125	7	2256	3	2324	6	2253	9	2324	6	CH ₂ asymm str
41	3068	4	3185	21	3068	4	3185	21	3065	4	3185	21	3065	10	3185	21	CH str
42	3105	3	3194	10	3106	4	3194	10	3104	8	3194	10	3104	10	3194	10	CH str

[a] Argon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the B3LYP-D/6-311++G(2d,2p) level of theory (unscaled). The assignment is based on band positions and intensities. [d] Calculated intensities in km/mol .

Table S4. Experimental and calculated [B3LYP-D/TZVPP//CHARMM] IR vibrations (cm⁻¹) of conformer **2-anti** and its different isotopomers

2-anti B3LYP-D/TZVPP//CHARMM													
mode	H-O ¹⁶			H-O ¹⁸			D-O ¹⁶			D-O ¹⁸			assignments
	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	^a v _{Exp}	^b Int _{Exp}	^c v _{Cal}	
8	501	10	513	499	9	510	491	23	504	-	-	501	C-CH2 oop
9	607	40		603	53		593	38		589	46		CH/ CH ₂ oop
	608	5	618	605	9	615	595	11	604	591	33	600	
11	695	73		695	73		694	40		694	43		CH oop
	-	-	716	-	-	716	695	100	716	695	93	716	
12	742	11		742	7		738	12		737	38		CH oop
	748	100	767	746	100	764	742	80	761	741	100	759	
13	831	10		-	-		-	-		-	-		CC/ C-CH ₂ str Ring def
	836	36	839	834	38	836	792	14	803	790	18	799	
15	897	19		889	13		-	-		-	-		CH/CO oop
	900	7	905	894	7	893	-	-	893	-	-	878	
21	1029	4	1046	1028	6	1046	1022	34	1039	1020	32	1038	CH bend
24	1122	14	1185	1061	9	1119	1126	21	1187	1062	17	1122	OO str
27	1206	5		1222	5		1259	15		1258	13		-
	1211	9	1236	-	-	1236	1264	21	1273	1266	53	1271	
30	1350	23		1346	18		1023	42		1022	27		CH ₂ wagging
	1354	9	1375	1351	14	1372	1024	40	1053	1023	69	1051	
31	1356	7		-	-		1025	-		-	-		-
	-	-	1484	-	-	1484	1039	22	1089	1037	33	1088	
32	1456	6		1460	10		1040	20		1039	25		CC str./CH bend
	1460	6	1486	-	-	1486	1453	28	1481	1455	57	1481	
33	1503	4		1503	12		1503	14		1502	19		CC str./CH bend
	-	-	1530	-	-	1530	1504	21	1529	1503	26	1529	
36	2973	3	3031	2973	3	3051	2177	4	2217	2177	8	2217	CH ₂ symm str
37	3046	5	3116	3046	7	3116	2256	3	2318	2253	9	2318	CH ₂ asymm str
41	3068	4	3189	3068	4	3189	3065	4	3189	3065	10	3189	CH str
42	3105	3	3196	3106	4	3196	3104	8	3196	3104	10	3196	CH str

[a] Argon, 3 K. [b] Relative intensities based on the strongest absorption. [c] Calculated at the M06-2X/6-311++G(2d,2p) level of theory (unscaled). The assignment is based on band positions and intensity.

Table S5. Experimental and calculated frequencies for conformers **2-anti** and **2-gauche** compared to **2a** and **2b**. All frequencies are in cm^{-1} .

Mode	$\nu_{\text{exp}}^{[\text{a}]}$ 2a	$\nu_{\text{cal}}^{[\text{b}]}$ 2-anti	Mode	$\nu_{\text{exp}}^{[\text{a}]}$ 2b	$\nu_{\text{cal}}^{[\text{b}]}$ 2-gauche
8	501	508	8	522	510
9	607	617	9	608	613
11	608	705	11	694	706
12	695	757	12	697	758
13	742	837	13	733	827
15	748	899	14	736	838
21	831	1048	20	752	1020
23	836	1183	21	891	1049
27	897	1236	22	1016	1110
30	900	1371	23	1032	1159
31	1029	1490	26	1080	1230
33	1122	1533	28	1115	1334
36	1206	3065	30	1216	1370
37	1211	3123	29	1251	1360
41	1236	3185	31	1304	1484
42	1350	3194	32	1332	1490
	1354		33	1353	1531
	1356		36	1430	3070
	1456		37	1459	3130
	1460		38	1500	3162
	1503		40	2955	3180
	2973		41	2994	3188
	3046		42	3039	3196
	3068			3078	
	3105			3083	
				3097	

[a] Ar matrix 3K. [b] B3LYP-D/6-311++G(2d,2p), unscaled.

III. Calculated complexes, energies, IRC plot and computed vibrations

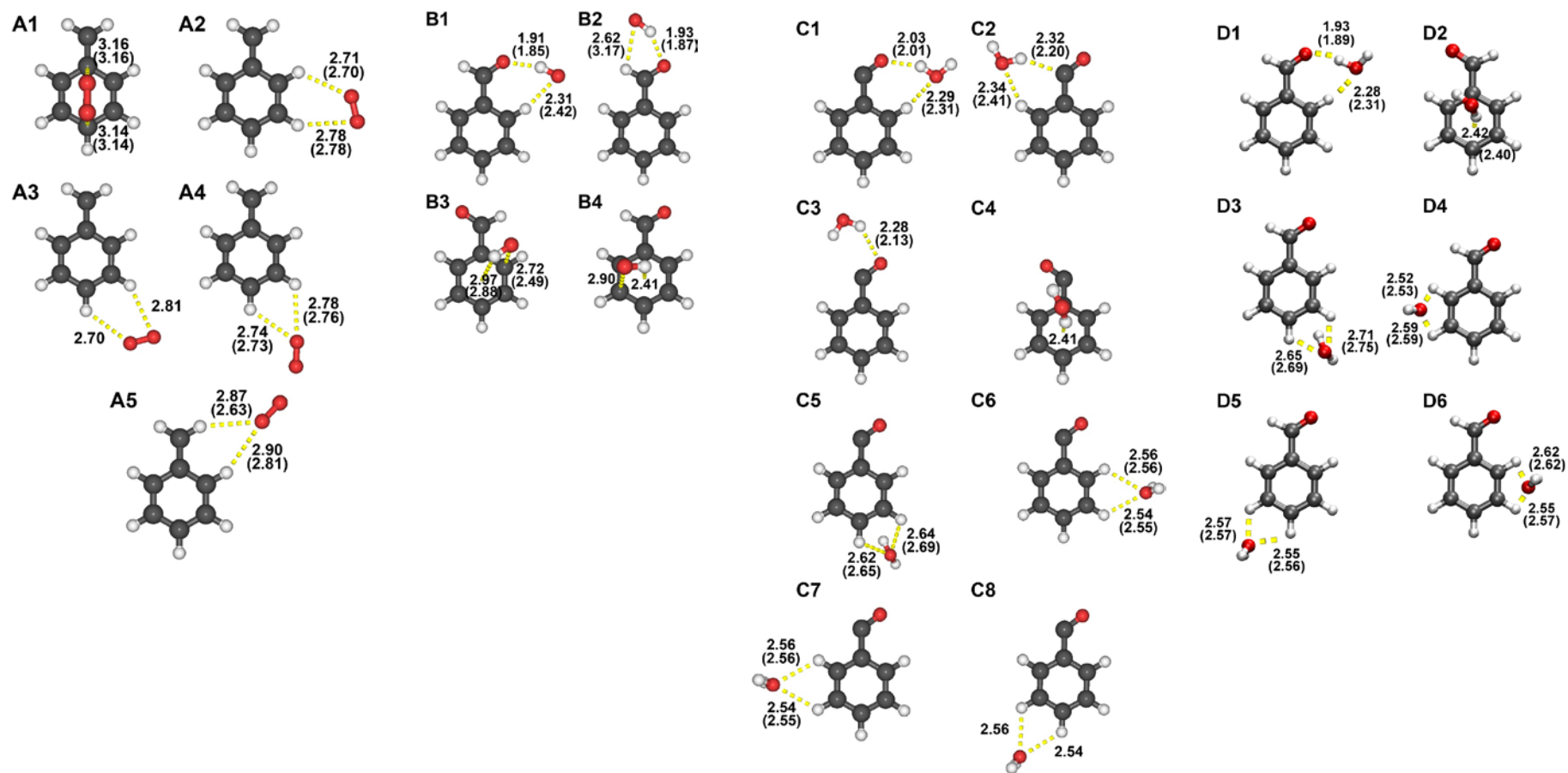


Figure S9. **A.** Calculated complexes between benzyl radical and oxygen. **B.** Complexes between benzaldehyde and hydroxyl radical. **C.** Complexes between benzoyl radical and water. **D.** Complexes between benzaldehyde and water. UM06-2X and UB3LYP-D (parenthesis) distances are shown in Å

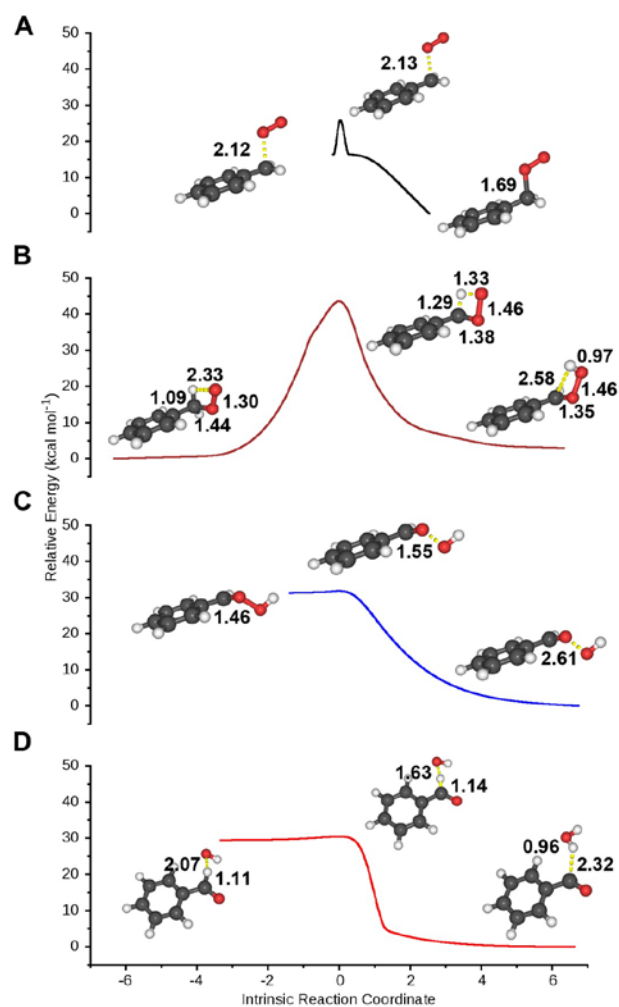


Figure S10. Intrinsic Reaction Coordinates plot for the four transition states connecting oxygen and benzyl radical with water and benzoyl radical. All distances are in Å. All energies and distances refer to the optimization with the UM06-2X functional.

Table S5. Stabilization Energies (ΔE) and Basis Set Superposition Error corrected Stabilization Energies (ΔE_{BSSE}) corresponding to the structures shown in **Figure S8**. Superscripts M, CCSD(T) and B refer to UM06-2X, UCCSD(T) and UB3LYP-D energies. All energies are in kcal·mol⁻¹.

Complex	ΔE^{M}	$\Delta E_{\text{BSSE}}^{\text{M}}$	$\Delta E^{\text{CCSD(T)}}$	ΔE^{B}	$\Delta E_{\text{BSSE}}^{\text{B}}$
A1	-2.7	-2.2	-1.4	-2.1	-1.6
A2	-0.8	-0.5	-1.3	-0.9	-0.6
A3	-0.8	-0.5	-1.2	-	-
A4	-0.7	-0.4	-1.2	-0.8	-0.5
A5	-0.6	-0.3	-1.1	-0.7	-0.4
B1	-6.9	-6.5	-6.3	-7.7	-7.3
B2	-6.6	-6.2	-5.8	-7.0	-6.7
B3	-4.8	-4.3	-3.4	-5.3	-4.8
B4	-4.5	-4.1	-3.2	-	-
C1	-5.3	-4.9	-5.3	-5.8	-5.5
C2	-5.0	-4.7	-4.3	-5.3	-4.9
C3	-3.4	-3.1	-3.0	-3.7	-3.4
C4	-3.1	-2.7	-3.0	-	-
C5	-2.9	-2.6	-2.6	-3.0	-2.7
C6	-2.8	-2.6	-2.9	-2.9	-2.6
C7	-2.8	-2.5	-2.9	-2.8	-2.5
C8	-2.8	-2.5	-2.8	-	-
D1	-6.6	-6.3	-6.7	-7.4	-7.0
D2	-3.5	-3.1	-3.4	-3.6	-3.1
D3	-2.8	-2.6	-2.6	-3.0	-2.8
D4	-2.8	-2.5	-2.9	-2.8	-2.5
D5	-2.6	-2.4	-2.7	-2.7	-2.4
D6	-2.6	-2.3	-2.7	-2.7	-2.4

Table S6. Calculated frequencies (cm^{-1}) and intensities (KM/mol) of the complexes between benzyl radical and oxygen at the B3LYP-D level of theory.

B3LYP									
A1		A2		A3		A4		A5	
V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int
42	0	17	0			17	0	13	0
58	0	18	0			18	0	16	0
70	0	20	0			33	0	16	0
87	1	38	0			35	0	22	0
123	1	68	0			54	0	61	0
203	2	197	1			198	1	197	1
362	0	362	0			362	0	365	0
392	0	395	0			395	0	397	0
476	18	482	16			477	16	479	16
528	0	517	0			517	0	515	0
534	1	534	0			535	0	535	0
627	0	629	0			629	0	628	0
678	39	686	55			682	51	688	59
730	0	718	3			718	2	719	4
782	68	781	53			778	58	787	48
829	0	830	0			830	1	830	0
832	0	831	0			832	0	832	0
906	4	905	6			902	6	905	6
979	2	977	2			976	2	980	2
983	0	980	0			980	0	981	0
991	0	992	0			989	0	994	0
996	1	996	1	-	-	996	2	996	2
1031	2	1033	3			1031	3	1031	3
1117	2	1116	4			1116	3	1116	2
1175	0	1174	0			1174	1	1173	0
1184	2	1184	0			1184	1	1184	0
1293	3	1288	1			1288	1	1288	1
1326	0	1320	1			1320	1	1320	1
1358	1	1358	1			1358	0	1358	0
1476	6	1476	6			1475	5	1475	5
1497	1	1495	0			1495	0	1497	1
1507	18	1504	12			1505	12	1506	9
1569	1	1571	1			1571	2	1571	1
1580	89	1590	1			1589	1	1590	1
1593	10	1625	0			1624	2	1626	0
3142	5	3141	6			3141	5	3146	4
3162	6	3161	4			3162	6	3160	6
3164	1	3170	2			3165	3	3164	0
3176	4	3176	8			3177	7	3176	10
3181	29	3183	27			3182	27	3181	26
3194	9	3194	11			3196	11	3192	12
3239	7	3239	7			3239	7	3246	5

Table S7. Calculated frequencies (cm⁻¹) and intensities (KM/mol) of the complexes between benzaldehyde and hydroxyl radical at the B3LYP-D level of theory.

B3LYP-D							
B1		B2		B3		B4	
VCal	Int	VCal	Int	VCal	Int	VCal	Int
23	1	26	3	37	1		
69	4	29	1	70	0		
122	1	120	1	109	7		
160	6	141	1	124	25		
243	3	241	8	176	33		
256	15	255	32	221	10		
414	4	412	0	249	10		
445	34	450	6	417	0		
448	45	462	12	439	0		
470	59	502	177	455	11		
619	87	594	86	490	126		
632	12	631	0	630	2		
670	66	668	30	660	21		
700	44	686	19	699	14		
766	44	760	60	755	64		
840	32	845	29	834	32		
862	3	864	0	869	1		
948	4	947	2	943	7		
1000	2	999	0	998	2		
1016	2	1013	0	1013	1		
1020	1	1016	1	1014	2		
1037	3	1037	1	1026	2		
1043	2	1041	3	1039	4		
1110	3	1101	4	1095	4		
1186	1	1185	3	1181	22		
1201	36	1190	31	1188	7		
1226	58	1230	67	1216	50		
1334	20	1334	19	1330	11		
1363	9	1354	9	1351	6		
1432	5	1433	6	1422	4		
1488	16	1489	17	1483	11		
1528	1	1525	2	1520	0		
1613	16	1615	23	1607	19		
1633	55	1633	55	1620	20		
1737	374	1737	401	1763	263		
2920	93	2920	59	2926	69		
3162	3	3164	2	3171	1		
3173	2	3173	1	3182	5		
3182	8	3184	8	3189	4		
3190	4	3194	8	3197	5		
3197	15	3200	8	3200	10		
3499	390	3490	707	3743	32		

Table S8 Calculated frequencies (cm^{-1}) and intensities (KM/mol) of the complexes between benzoyl radical and water at the B3LYP-D level of theory.

B3LYP-D															
C1		C2		C3		C4		C5		C6		C7		C8	
V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int
37	0	39	0	-5.77	0			8	8	11	12	16	10		
82	109	69	19	18	1			44	4	34	3	36	2		
84	18	91	93	65	83			103	11	92	22	101	7		
110	1	117	3	106	2			115	25	102	59	106	14		
129	6	122	15	113	3			130	146	105	6	121	27		
229	7	212	7	206	33			175	158	128	179	136	210		
248	6	237	28	232	47			196	29	140	25	137	20		
301	112	325	103	245	0			211	3	214	0	212	4		
415	5	414	10	397	114			244	6	239	0	237	0		
443	2	443	15	413	0			419	1	417	0	417	0		
452	105	449	54	445	1			441	0	442	0	442	0		
479	35	495	19	468	1			470	3	476	3	476	3		
624	9	624	6	625	9			624	11	624	10	624	9		
637	18	638	13	638	21			636	12	636	14	636	14		
704	34	705	32	696	26			703	23	703	25	702	24		
773	50	773	52	765	58			777	66	773	58	772	58		
808	16	809	14	812	17			804	16	807	16	806	16		
869	0	868	0	862	0			871	0	875	0	875	1		
966	3	967	4	956	3			963	2	962	3	964	4		
1008	0	1007	0	999	0			1005	0	1006	0	1007	0		
1016	1	1016	1	1017	0			1015	1	1018	1	1017	1		
1026	0	1026	0	1017	1			1029	0	1033	0	1032	0		
1043	3	1045	3	1043	4			1043	3	1038	4	1038	4		
1106	6	1105	4	1099	5			1098	6	1097	10	1097	11		
1167	69	1166	78	1165	74			1157	66	1157	63	1157	66		
1186	3	1186	1	1186	1			1188	2	1182	0	1182	0		
1209	0	1208	1	1202	2			1200	1	1197	5	1198	3		
1323	9	1325	7	1326	7			1324	7	1324	8	1324	7		
1362	6	1363	2	1352	5			1352	4	1345	8	1346	8		
1479	13	1481	14	1481	14			1481	13	1478	17	1478	17		
1520	1	1519	1	1515	0			1514	1	1511	0	1512	0		
1608	6	1610	13	1609	15			1609	10	1608	13	1610	10		
1625	22	1625	13	1625	23			1624	20	1623	13	1622	16		
1653	95	1646	53	1658	146			1635	93	1641	83	1640	83		
1860	370	1872	296	1861	356			1873	299	1869	301	1867	309		
3170	2	3169	1	3171	0			3175	1	3167	2	3166	3		
3180	6	3181	9	3180	2			3181	1	3179	6	3180	9		
3186	12	3188	5	3187	5			3189	1	3191	11	3191	8		
3195	1	3196	2	3195	8			3194	8	3199	5	3198	3		
3198	30	3199	17	3199	8			3200	3	3213	2	3208	2		
3741	209	3641	288	3783	169			3804	8	3815	14	3815	14		
3895	123	3877	93	3896	96			3908	97	3916	71	3917	72		

Table S9. Calculated frequencies (cm⁻¹) and intensities (KM/mol) for the complexes between benzaldehyde and water at the B3LYP-D level of theory

B3LYP-D											
D1		D2		D3		D4		D5		D6	
V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int	V _{Cal}	Int
38	0	32	1	6	8	-19	0	-21	0	16	6
86	10	44	1	40	6	35	1	37	0	27	1
105	115	107	6	105	72	105	1	101	53	93	99
122	2	114	7	114	89	114	1	103	1	96	42
150	9	127	6	123	23	118	53	123	1	117	1
244	4	152	104	186	66	128	7	127	219	126	190
250	15	201	78	188	131	130	206	133	7	153	23
382	125	221	11	222	5	224	10	222	8	224	2
418	6	239	6	245	10	237	7	239	10	236	9
447	2	415	0	421	1	418	0	419	0	418	0
466	7	441	0	442	0	443	0	444	0	444	0
589	107	464	7	466	7	470	7	465	7	470	7
631	1	631	0	631	0	631	0	632	0	631	1
667	31	662	23	662	24	664	25	662	26	663	24
705	41	699	22	703	23	704	25	705	23	704	26
767	42	764	55	770	59	767	53	774	55	766	51
840	31	837	33	837	33	839	33	838	30	840	32
866	0	870	0	872	1	876	0	870	0	874	0
951	1	946	1	950	0	953	2	953	1	948	1
1003	0	1003	0	1004	0	1009	0	1007	0	1003	0
1016	1	1014	0	1015	1	1017	2	1017	1	1018	1
1022	0	1016	1	1026	0	1023	0	1030	1	1027	1
1041	1	1032	1	1034	1	1036	1	1037	0	1036	4
1043	2	1041	3	1041	3	1037	4	1042	4	1041	1
1111	4	1098	4	1099	5	1099	8	1096	6	1098	10
1186	1	1184	5	1187	4	1181	1	1181	13	1179	12
1202	42	1188	27	1188	29	1184	35	1185	20	1184	19
1225	52	1220	53	1220	57	1222	56	1221	74	1222	57
1334	20	1329	15	1330	18	1330	17	1331	12	1331	19
1363	12	1351	8	1352	7	1348	10	1351	7	1347	9
1435	4	1425	5	1423	5	1423	6	1424	5	1421	6
1488	16	1488	13	1489	14	1486	17	1485	13	1486	17
1528	0	1523	0	1523	1	1520	1	1522	0	1520	1
1614	13	1614	15	1615	12	1616	12	1614	19	1615	16
1632	42	1632	25	1631	38	1630	35	1631	37	1631	25
1667	113	1646	101	1637	79	1640	79	1640	91	1642	83
1743	369	1764	271	1762	291	1757	307	1756	305	1756	298
2909	97	2892	97	2880	111	2879	112	2876	115	2875	117
3161	4	3168	2	3161	4	3166	3	3158	8	3157	4
3172	2	3176	1	3177	1	3180	1	3171	5	3170	8
3185	16	3185	6	3184	6	3181	11	3193	0	3187	14
3194	8	3194	6	3193	5	3194	7	3196	11	3199	5
3208	23	3199	8	3199	3	3202	5	3206	1	3214	1
3656	446	3807	45	3804	16	3815	14	3814	14	3815	14
3892	97	3902	62	3908	114	3916	72	3916	71	3916	68

IV. Photochemistry of the benzylperoxy radical at 365 nm

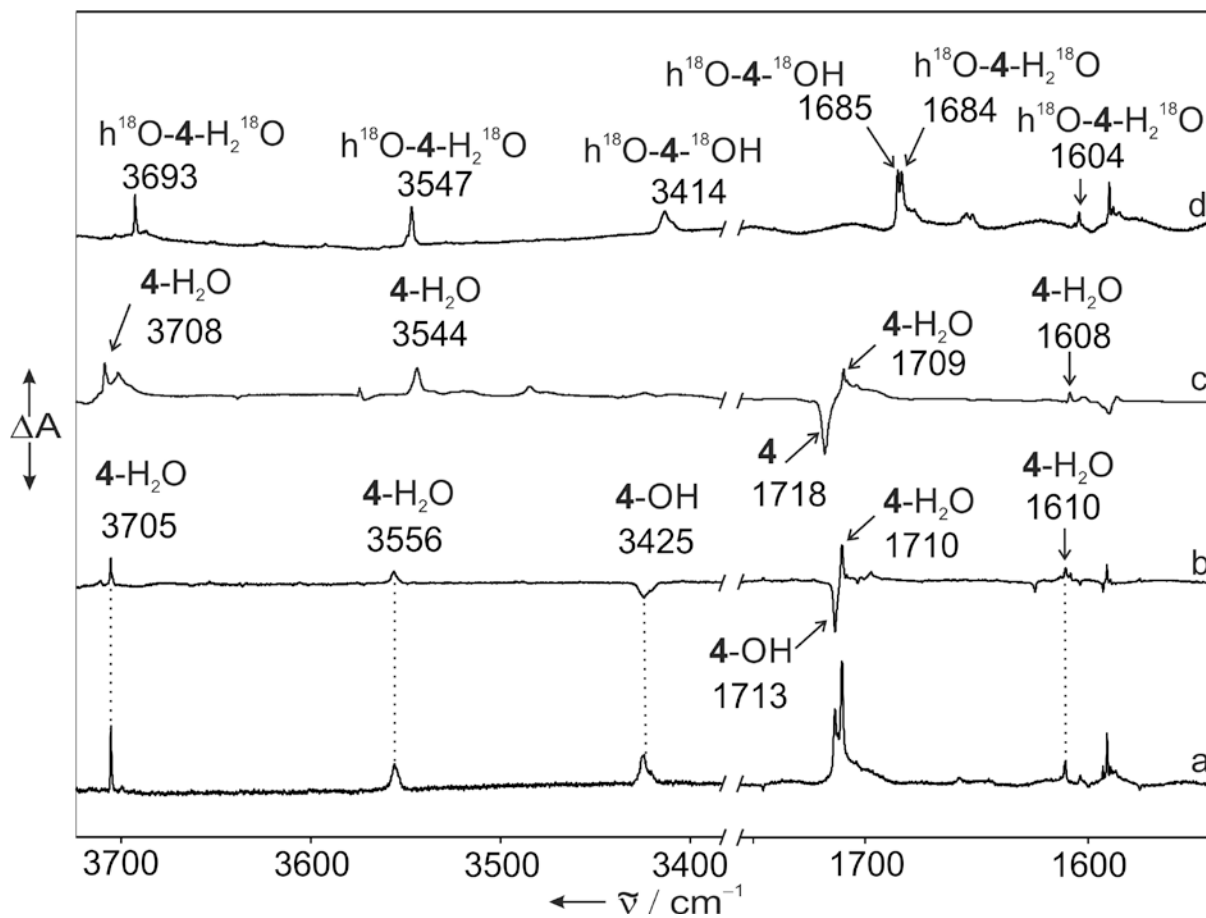


Figure S11. Difference IR spectra showing the photochemistry of $2\text{-h}_2^{16}\text{O}_2$ and $2\text{-h}_2^{18}\text{O}_2$ in argon at 3 K. Bands pointing upwards are appearing and bands pointing downwards are disappearing during the experiments. (a) Difference spectrum obtained after irradiating the deposited spectrum of $2\text{-h}_2^{16}\text{O}_2$ at 365 nm for 10 min at 3 K. (b) Same matrix, warming from 3 K to 25 K. (c) Reference spectrum of benzaldehyde **4**, matrix-isolated in 1% H_2O -doped argon. Difference of the spectra taken at 3 K and taken after warming to 30 K, showing the formation of the **4**- H_2O complex. (d) Difference spectrum obtained after irradiating the deposited spectrum of $2\text{-h}_2^{18}\text{O}_2$ at 365 nm for 10 min at 3 K.

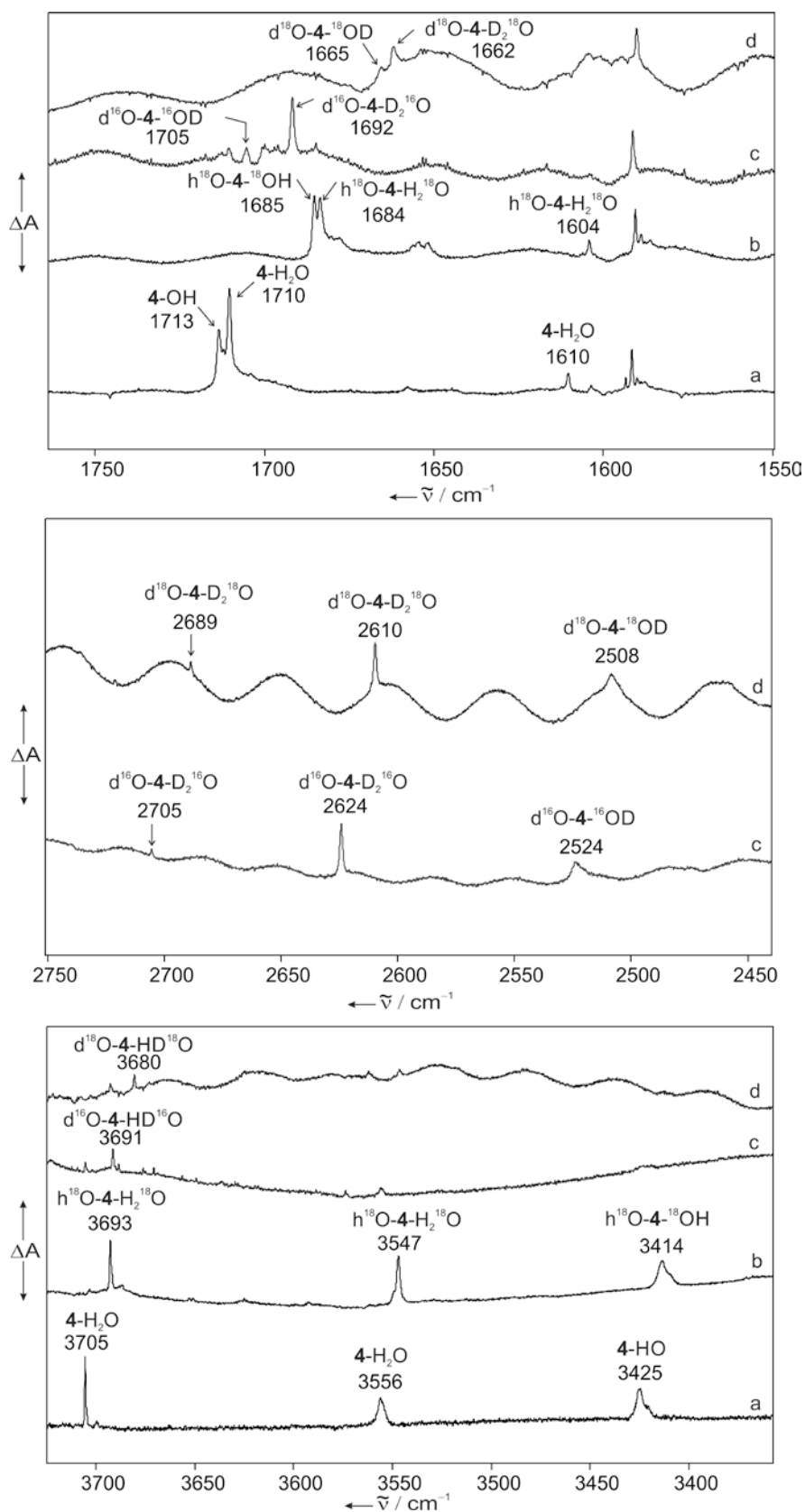


Figure S12. Difference IR spectra showing the photochemistry of benzylperoxy radical ($2\text{-h}_2^{16}\text{O}_2$) and several isotopomers ($2\text{-h}_2^{18}\text{O}_2$, $2\text{-d}_2^{16}\text{O}_2$, and $2\text{-d}_2^{18}\text{O}_2$) in argon at 3 K. Bands pointing upwards are appearing and bands pointing downwards are disappearing during the experiments. Difference spectrum obtained after irradiating the deposited spectrum of **2** at 365 nm for 10 min at 3 K. (a) $2\text{-h}_2^{16}\text{O}_2$ (b) $2\text{-h}_2^{18}\text{O}_2$ (c) $2\text{-d}_2^{16}\text{O}_2$ (d) $2\text{-d}_2^{18}\text{O}_2$.

V. Long time photochemistry with 365-320 nm

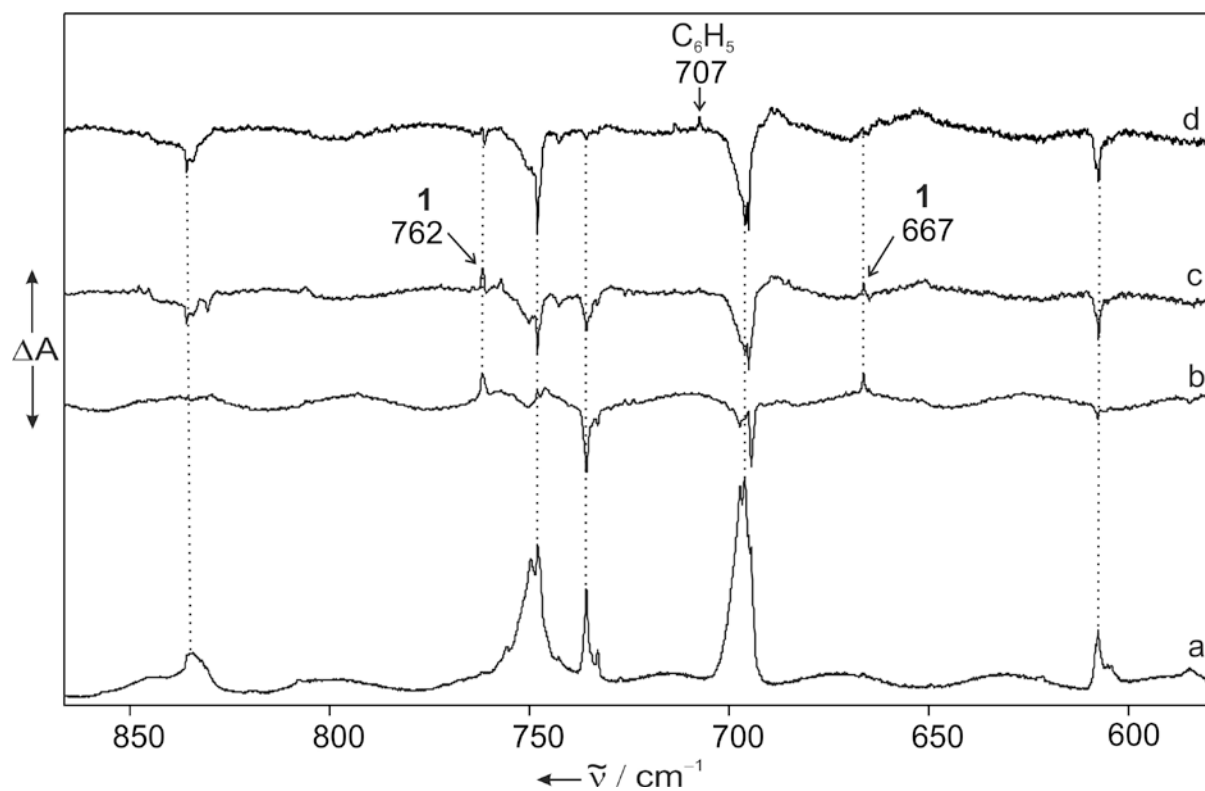


Figure S13. Difference IR spectra in this region 600-900 cm^{-1} showing the photochemistry of benzylperoxy radical ($2\text{-h}_2^{16}\text{O}_2$) in argon at 3 K. Bands pointing upwards are appearing and bands pointing downwards are disappearing during photolysis. (a) Deposition spectrum of $2\text{-h}_2^{16}\text{O}_2$ at 3 K. Same matrix as (a) after (b) 60 min irradiation at $\lambda = 365$ nm, (c) several hours irradiation at $\lambda = 365$ nm, (d) several hours irradiation at $\lambda = 320$ nm.

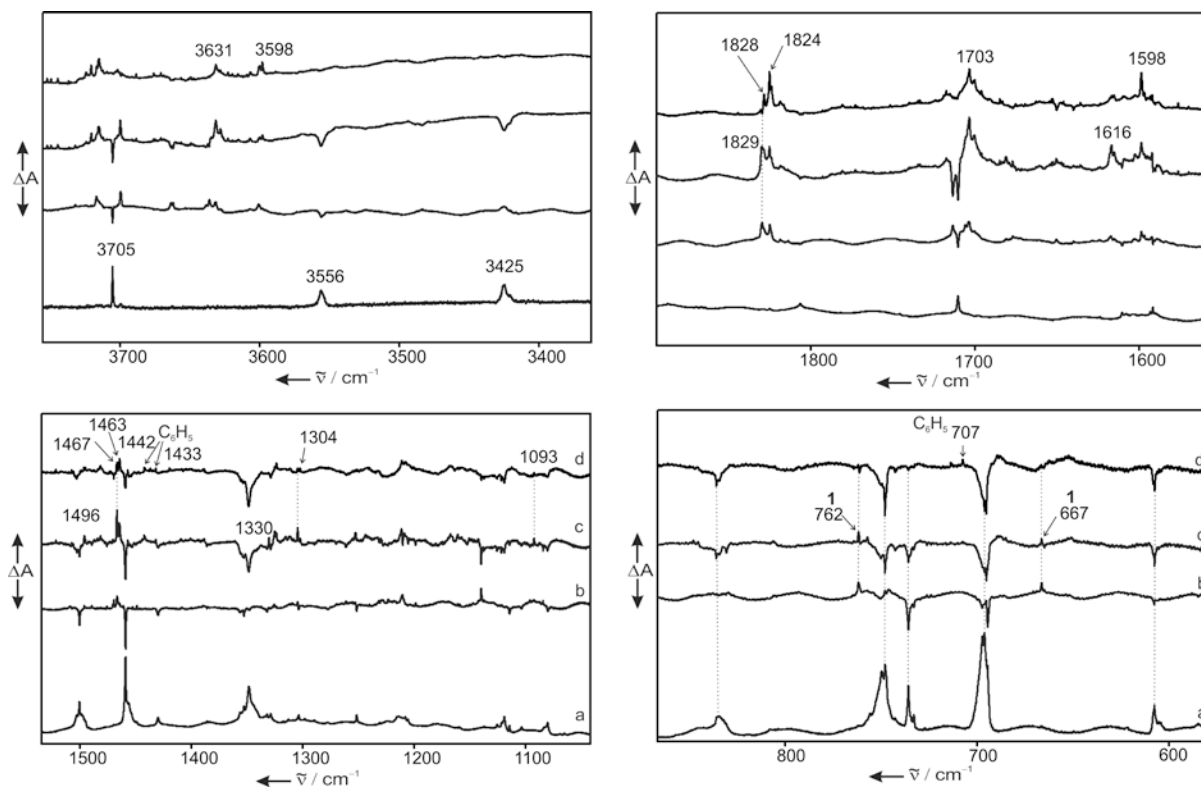


Figure S14. Difference IR spectra showing the photochemistry of benzylperoxy radical ($2\text{-h}_2^{16}\text{O}_2$) in argon at 3 K. Bands pointing upwards are appearing and bands pointing downwards are disappearing during photolysis. (a) Deposition spectrum of $2\text{-h}_2^{16}\text{O}_2$ at 3 K. Same matrix as (a) after (b) 60 min irradiation at $\lambda = 365$ nm, (c) several hours irradiation at $\lambda = 365$ nm, (d) Several hours irradiation at $\lambda = 320$ nm.