

**Supporting Information Table 1.** The molecular geometries, rotational constants (GHz) and harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) for  $\text{CH}_3\text{OOH}$ ,  $\text{CH}_3\text{OO}^-$ , and  $\tilde{X}$  and  $\tilde{A}$  states of the neutral  $\text{CH}_3\text{OO}$  radicals, calculated at the B3LYP/aug-cc-pVDZ level of theory. Rotational constants and vibrational frequencies given in parentheses represent the values for the  $\text{d}_3$ -isotopomers. All vibrational frequencies are unscaled.

	$\text{CH}_3\text{OO}^-$	$\text{CH}_3\text{OO}$	$\text{CH}_3\text{OO}$	$\text{CH}_3\text{OOH}$	
<b>Molecular Geometries (<math>\text{\AA}</math>, <math>^\circ</math>)</b>					
	$C_s (\tilde{X}, ^1A')$	$C_s (\tilde{X}, ^2A'')$	$C_s (\tilde{A}, ^2A')$	$C_1$	
$r_e[\text{H}_3\text{C-OO}]$	1.387	1.452	1.440	1.420	
$r_e[\text{H}_3\text{CO-O}]$	1.476	1.317	1.385	1.454	
$\angle[\text{H}_3\text{C-O-O}]$	106.2	111.2	107.6	106.4	
<b>Rotational Constants (GHz)</b>					
A	45.7 (34.9)	52.5 (39.0)	52.4 (47.7)	43.1 (33.4)	
B	11.2 (9.5)	11.3 (9.5)	11.2 (11.3)	10.4 (8.9)	
C	9.5 (8.2)	9.9 (8.5)	9.8 (9.7)	9.1 (7.9)	
<b>Vibrational Frequencies (<math>\text{cm}^{-1}</math>)</b>					
	<b>a'</b> modes			<b>a</b> modes	
$\omega_1$	2938 (2176)	3166 (2353)	3157 (2342)	$\omega_1$	3754 (3754)
$\omega_2$	2874 (2057)	3052 (2182)	3025 (2164)	$\omega_2$	3121 (2315)
$\omega_3$	1463 (1147)	1451 (1203)	1475 (1087)	$\omega_3$	3089 (2293)
$\omega_4$	1390 (1053)	1414 (1070)	1419 (1069)	$\omega_4$	3012 (2156)
$\omega_5$	1188 (1012)	1211 (1045)	1157 (1007)	$\omega_5$	1478 (1364)
$\omega_6$	1074 (945)	1149 (985)	1015 (950)	$\omega_6$	1430 (1123)
$\omega_7$	806 (764)	910 (825)	917 (836)	$\omega_7$	1419 (1058)
$\omega_8$	428 (387)	491 (444)	370 (343)	$\omega_8$	1367 (1035)

a''			a		
modes				modes	
$\omega_9$	2885 (2139)	3152 (2342)	3104 (2306)	$\omega_9$	1192 (1014)
$\omega_{10}$	1394 (1015)	1440 (1040)	1432 (1037)	$\omega_{10}$	1153 (974)
$\omega_{11}$	1145 (886)	1111 (853)	1150 (884)	$\omega_{11}$	1029 (891)
$\omega_{12}$	271 (207)	129 (101)	247 (192)	$\omega_{12}$	875 (809)
				$\omega_{13}$	444 (402)
				$\omega_{14}$	245 (192)
				$\omega_{15}$	175 (169)



**Supporting Information Table 2.** The molecular geometries, rotational constants (GHz), and harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) for  $\text{CH}_3\text{CH}_2\text{OOH}$ ,  $\text{CH}_3\text{CH}_2\text{OO}^-$  and  $\tilde{X}$  and  $\tilde{A}$  states of the neutral  $\text{CH}_3\text{CH}_2\text{OO}$  radicals, calculated at the B3LYP/aug-cc-pVDZ level of theory. All vibrational frequencies are unscaled.

	$\text{CH}_3\text{CH}_2\text{OO}^-$	$\text{CH}_3\text{CH}_2\text{OO}$	$\text{CH}_3\text{CH}_2\text{OO}$	$\text{CH}_3\text{CH}_2\text{OOH}$
<b>Molecular Geometries (<math>\text{\AA}</math>, <math>^\circ</math>)</b>				
	$C_s (\tilde{X}, ^1A')$	$C_s (\tilde{X}, ^2A'')$	$C_s (\tilde{A}, ^2A')$	$C_1$
$r_e[\text{CH}_3\text{H}_2\text{C}-\text{OO}]$	1.388	1.467	1.453	1.430
$r_e[\text{CH}_3\text{H}_2\text{CO}-\text{O}]$	1.477	1.316	1.383	1.452
$r_e[\text{H}_3\text{C}-\text{CH}_2\text{OO}]$	1.532	1.515	1.517	1.521
$\angle[\text{CH}_3\text{H}_2\text{C}-\text{O}-\text{O}]$	106.9	111.6	108.1	106.9
<b>Rotational Constants (GHz)</b>				
A	33.3	33.3	32.4	30.9
B	4.2	4.4	4.4	4.1
C	4.0	4.1	4.1	3.9
<b>Vibrational Frequencies (<math>\text{cm}^{-1}</math>)</b>				
$a'$ modes				$a$ modes
$\omega_1$	3065	3122	3123	$\omega_1$ 3753
$\omega_2$	3002	3067	3048	$\omega_2$ 3125
$\omega_3$	2878	3047	3032	$\omega_3$ 3119
$\omega_4$	1485	1479	1500	$\omega_4$ 3062
$\omega_5$	1464	1469	1474	$\omega_5$ 3044
$\omega_6$	1354	1396	1391	$\omega_6$ 3015
$\omega_7$	1325	1354	1361	$\omega_7$ 1502

$\omega_8$	1181	1199	1111	$\omega_8$	1473
$\omega_9$	1045	1125	1018	$\omega_9$	1454
$\omega_{10}$	908	1016	999	$\omega_{10}$	1396
$\omega_{11}$	816	831	841	$\omega_{11}$	1368
$\omega_{12}$	465	501	427	$\omega_{12}$	1356
$\omega_{13}$	291	305	279	$\omega_{13}$	1258
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a'' modes				a modes	
$\omega_{14}$	3075	3137	3136	$\omega_{14}$	1169
$\omega_{15}$	2872	3116	3079	$\omega_{15}$	1142
$\omega_{16}$	1441	1456	1452	$\omega_{16}$	1043
$\omega_{17}$	1220	1259	1259	$\omega_{17}$	946
$\omega_{18}$	1163	1134	1167	$\omega_{18}$	862
$\omega_{19}$	789	794	825	$\omega_{19}$	819
$\omega_{20}$	220	215	225	$\omega_{20}$	474
$\omega_{21}$	122	71	120	$\omega_{21}$	294
				$\omega_{22}$	230
				$\omega_{23}$	188
				$\omega_{24}$	124

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