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Suplimentary Information for

Revisiting the reaction of $CH_3O^\bullet$ with O_2 ($^3\Sigma^-$): Crucial role of post-CCSD(T) corrections

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Sl. No.	Contents
1	**Table S1** :Comparison of frequencies in (cm^{-1}) and geometrical parameters of relevant structures obtained in present work (CCSD(T)/cc-pVTZ) with available experimental value.
2	**Table S2**:Optimized geometries in cartesian coordinates and all normal mode frequencies calculated at the CCSD(T)/cc-pVTZ level of theory.
3	**Table S3** :Harmonic and anharmonic frequencies of all relevant species in cm^{-1} obtained at X3LYP/6-311G** level of theory
4	**Table S4** :Comparison of rate coefficients in ($cm^{3}\ s^{-1}$) for the title reaction, obtained at Transition state theory ($k^{har}{}_{TST/ZCT}$ and $k^{anhar}{}_{TST/ZCT}$) with experimental results (k_{EXPT}) within temperature range 250-900 K.
5	**Table S5** : Absolute electronic energies calculated at the CCSD(T)/aug-cc-pVTZ, CCSD(T)/aug-cc-pVQZ and CCSD(T)/CBS levels of theory (in Hartree).
6	**Figure S1** :The optimised geometry of all the relevant structures obtained in present work at CCSD(T)/cc-pVTZ level of theory.

Table S1: Comparison of frequencies in (cm^{-1}) and geometrical parameters of relevant structures, obtained in present work (CCSD(T)/cc-pVTZ) with available experimental value.

Methods	Species	Frequencies (cm^{-1})	Bond length (Å)				Bond angle(°)		
			R_{C-H}	R_{C-O}	$R_{o=o}$	$R_{C=O}$	A_{O-C-H}	A_{H-C-H}	A_{H-O-O}
	$CH_3O^{\bullet}$	2840 , 914 , 1412 , 652 , 1047 , 2758	1.11	1.40			111.3	107.5	
Experimental	O_2	1580			1.20				
	CH_2O	2782, 2843, 1746, 1249, 1500, 1167	1.11			1.20	121.9	116.1	
	$HO_2^{\bullet}$	3436, 1098, 1392			1.33				104.2
	$CH_3O^{\bullet}$	767, 968, 1116, 1388, 1394	1.09	1.37			112.9	106.9	
		1524, 2943, 3019, 3061							
CCSD(T)/cc-pVTZ	O_2	1583			1.21				
	CH_2O	1192, 1274, 1543, 1780, 2929, 2995	1.10			1.20	121.9	116.1	
	$HO_2^{\bullet}$	965, 1234, 3760			1.40				101.3

Table S2: Optimized geometries in cartesian coordinates and all normal mode frequencies calculated at the CCSD(T)/cc-pVTZ level of theory.

Species	Cartesian coordinate (Å)				Frequencies (cm^{-1})
	O	0.00	0.00	0.00	1583.7144
O_2	O	0.00	0.00	1.21220899	
$CH_3O^\bullet$	O	0.00	0.00	0.00	767.1706 ,968.7224 ,1116.0596
	C	0.00	0.00	1.3759293	1388.9675, 1394.5491
	H	1.06465899	0.00	1.66557275	3019.4236, 3061.8177
	H	-0.44723026	0.90478626	1.80249964	1524.64, 2943.3706
	H	0.44723026	-0.90478626	1.80249964	
	C	0.00	0.00	0.00	138.1883, 218.2083, 355.1952,
	H	0.00	0.00	1.09166949	543.5466, 715.3618, 1035.2846
RC	H	1.02571485	0.00	-0.3697448	1174.4799, 1174.8368, 1292.6272
	H	-0.52721049	-0.88104732	-0.3708733	1432.0476, 1461.7779, 1516.5759
	O	-0.52463025	1.19712883	-0.53204361	3033.7796, 3114.1488, 3139.2639
	O	-1.98291766	1.33180643	-0.08749799	
	O	-2.38959811	0.38675369	0.62840744	
	O	0.00	0.00	0.00	190.9349,252.2367,491.4389
	O	0.00	0.00	1.22611051	582.6105,688.9518,1151.2018
	H	1.39566772	0.00	1.4667326	1232.365,1269.7968,1358.1544
TS	C	2.45670082	0.00	0.82181902	-1444.0995, 1491.155, 1540.7782
	H	2.91495565	0.92733864	1.19325261	1653.3144, 2958.4909, 3038.2652
	H	2.91495565	-0.92733864	1.19325261	
	O	2.00588831	0.00	-0.39017308	
	O	1.513417	0.732443	0.000563	65.3088, 124.2180, 182.2915
	O	1.474768	-0.592465	-0.000612	198.8997 , 238.4886, 628.7308
	H	0.51594	-0.787653	0.000399	1194.9596, 1235.7616, 1296.4796
PC	C	-1.713399	0.47981	-0.000347	1552.3618, 1576.6435. 1804.4672
	H	-2.793936	0.673639	0.000157	3003.9705, 3102.1267, 3553.6631
	H	-1.037551	1.341939	-0.001876	
	O	-1.288693	-0.653326	0.000473	
	C	0.00	0.00	0.00	1192.1841, 1274.8661, 1543.1947
CH_2O	H	0.00	0.00	1.10327959	1780.7596, 2929.2275, 2995.8513
	H	0.99005364	0.00	-0.48684663	
	O	-1.02680409	0.00	-0.63931474	
	O	0.055939	-0.650222	0.00	965.8979, 1234.936, 3760.9185
$HO_2^\bullet$	H	-0.895022	-0.837408	0.00	
	O	0.055939	0.754898	0.00	

Table S3: Harmonic and anharmonic frequencies of all relevant species in cm^{-1} obtained at X3LYP/6-311G** level of theory

compound	harmonic	anharmonic	corr.-anharmonic
$CH_3O^\bullet$	702.718	702.718*	767.1706
	965.851	965.851*	968.7224
	1112.18	645.899	649.7786
	1373.61	1279.714	1295.0715
	1363.568	1339.923	1370.9041
	1519.384	1451.107	1456.363
	2896.878	2756.398	2802.8906
	2962.212	2752.761	2809.9726
	3003.197	2809.855	2868.4757
O_2	1580	-	-
RC	101.612	242.177	278.7533
	207.181	313.874	324.9013
	314.663	315.129	355.6612
	410.889	327.318	459.9756
	665.64	635.496	685.2178
	1019.271	1004.597	1020.6106
	1159.961	1137.55	1152.0689
	1169.879	1151.749	1156.7068
	1359.485	1354.493	1287.6352
	1429.151	1410.336	1413.2326
	1437.93	1416.036	1439.8839
	1510.904	1420.734	1426.4059
	2998.028	2781.611	2817.3626
	3066.263	2904.096	2951.9818
	3091.801	2933.215	2980.6779
TS	-1173.319	-1433.651	-1704.4315
	199.27	129.166	120.8309
	240.774	181.424	192.8867
	486.469	397.14	402.1099
	555.716	443.579	470.4735
	683.885	640.757	645.8238
	1107.13	1049.239	1093.3108
	1232.822	1231.861	1231.404
	1252.945	1223.565	1240.4168
	1361.968	1282.08	1278.2664
	1510.081	1490.117	1471.191
	1550.384	1507.78	1498.1742
	1652.535	1700.608	1701.3874
	2895.806	2719.134	2781.8189
	2967.009	2800.401	2871.6572

compound	harmonic	anharmonic	corr.-anharmonic
PC	79.745	73.942	59.5058
	136.019	115.8	103.999
	193.811	180.166	168.6465
	205.803	185.327	178.4237
	256.031	233.149	215.606
	642.701	573.598	559.6278
	1191.624	1165.894	1169.2296
	1222.01	1197.521	1211.2726
	1274.415	1246.678	1268.7426
	1524.339	1495.915	1523.9378
	1544.927	1491.591	1523.3075
	1787.739	1763.484	1780.2122
	2929.236	2763.923	2838.6575
	3028.578	2843.406	2916.9547
	3382.128	3187.823	3359.3281
CH_2O	1204.585	1184.78	1172.3791
	1272.121	1251.657	1254.4021
	1540.897	1508.675	1510.9727
	1832.391	1806.635	1755.0036
	2876.318	2673.464	2726.3735
	2926.962	2713.177	2782.0663
HO_2	1169.575	1145.901	942.2239
	1432.004	1396.398	1199.33
	3622.401	3401.326	3539.8435

*The VPT2 method is unable to calculate these anharmonic frequencies at X3LYP/6-311G** level of theory, so we assume these frequencies to be harmonic

Table S4: Comparison of rate coefficients in (cm ^{3} s^{-1}) for the title reaction, obtained at Transition state theory (k$^{har}{}_{TST/ZCT}$ and k$^{anhar}{}_{TST/ZCT}$) with experimental results (k$_{EXPT}$) within temperature range 250-900 K.

T(K)	$k^{har}_{TST/ZCT}$	$k^{anhar}_{TST/ZCT}$	k_{EXPT}
250	2.22×10^{-15}	3.09×10^{-15}	9.4×10^{-16} [a]
265	2.39×10^{-15}	3.35×10^{-15}	1.06×10^{-15} [a]
278	2.55×10^{-15}	3.60×10^{-15}	1.34×10^{-15} [a]
298	2.82×10^{-15}	4.03×10^{-15}	1.92×10^{-15} [b,c]
300	2.85×10^{-15}	4.07×10^{-15}	1.96×10^{-15} [b,c]
310	2.99×10^{-15}	4.31×10^{-15}	1.76×10^{-15}(316K) [a]
330	3.30×10^{-15}	4.80×10^{-15}	1.79×10^{-15}(333K) [a]
350	3.65×10^{-15}	5.35×10^{-15}	3.16×10^{-15} [b,c], 2.60×10^{-15} [d]
375	4.10×10^{-15}	6.06×10^{-15}	3.82×10^{-15} [b,c], 3.44×10^{-15} [d]
400	4.63×10^{-15}	6.95×10^{-15}	4.52×10^{-15} [b,c], 4.3×10^{-15} [d], 3.92×10^{-15} [e], 3.45×10^{-15} [f]
425	5.19×10^{-15}	7.87×10^{-15}	5.23×10^{-15} [b,c], 5.26×10^{-15} [d], 5.29×10^{-15} [e], 4.63×10^{-15} [f], 4.80×10^{-15} [g]
450	5.79×10^{-15}	8.89×10^{-15}	5.96×10^{-15} [b], 6.27×10^{-15} [d], 5.69×10^{-15} [g]
475	6.46×10^{-15}	9.99×10^{-15}	6.64×10^{-15} [g]
500	7.17×10^{-15}	11.20×10^{-15}	7.62×10^{-15} [g]
550	8.77×10^{-15}	13.92×10^{-15}	9.66×10^{-15} [g]
600	10.60×10^{-15}	17.07×10^{-15}	11.80×10^{-15} [g]
650	12.70×10^{-15}	20.70×10^{-15}	
700	1.50×10^{-14}	2.48×10^{-14}	1.61×10^{-14} [h]
725	1.63×10^{-14}	2.71×10^{-14}	1.72×10^{-14} [h]
750	1.77×10^{-14}	2.95×10^{-14}	1.82×10^{-14} [h]
775	1.91×10^{-14}	3.20×10^{-14}	1.93×10^{-14} [h]
800	2.07×10^{-14}	3.47×10^{-14}	2.03×10^{-14} [h]
825	2.23×10^{-14}	3.75×10^{-14}	2.14×10^{-14} [h]
850	2.40×10^{-14}	4.05×10^{-14}	2.24×10^{-14} [h]
875	2.58×10^{-14}	4.37×10^{-14}	2.34×10^{-14} [h]
900	2.76×10^{-14}	4.70×10^{-14}	2.44×10^{-14} [h]

[a] Chai et al., [b] Lorenz et.al , [c] Zellener et.al, [d] Cox et.al, [e] Batt et.al, [f] Barker et.al, [g] Gutman et.al [h] Zalonsko et.al

Table S5: Absolute electronic energies calculated at the CCSD(T)/aug-cc-pVTZ, CCSD(T)/aug-cc-pVQZ and CCSD(T)/CBS levels of theory (in Hartree)

Compounds	CCSD(T)/aug-cc-pVTZ	CCSD(T)/aug-cc-pVQZ	CCSD(T)/CBS
RC	-265.0242914	-265.0912339	-265.1330532339
TS	-265.0091164	-265.0761061	-265.1177769951
PC	-265.0848009	-265.1526196	-265.1944317268
CH_2O	-114.3429251	-114.3723672	-114.3907603106
$HO_2^\bullet$	-150.7239229	-150.76201	-150.7857377741
O_2	-150.1410187	-150.1786595	-150.2018360593
$CH_3O^\bullet$	-114.8851034	-114.913952	-114.9320006734

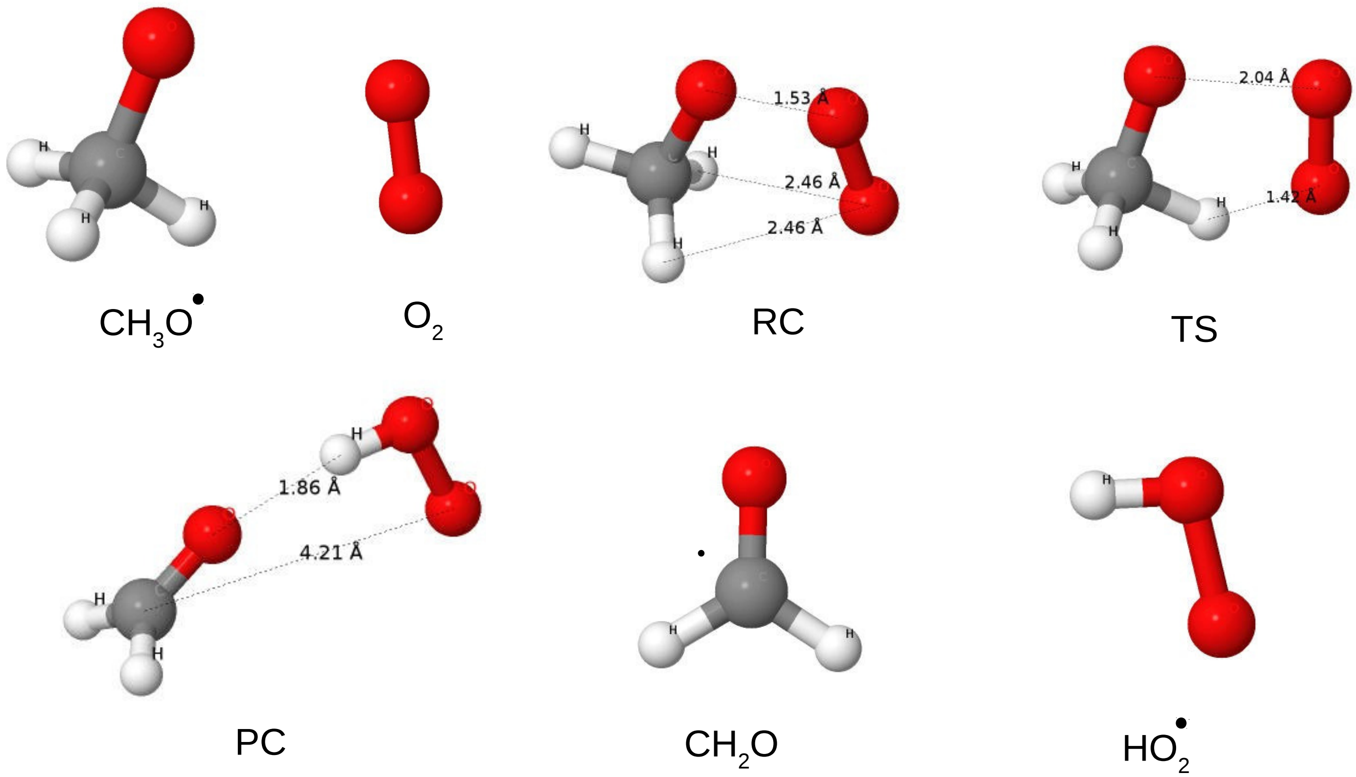

Figure S1: The optimised geometry of all the relevant structures obtained in present work at CCSD(T)/cc-pVTZ level of theory.