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Supplementary Information

A Combined High-Temperature Experimental and Theoretical Kinetic Study of Dimethyl Carbonate with OH Radicals

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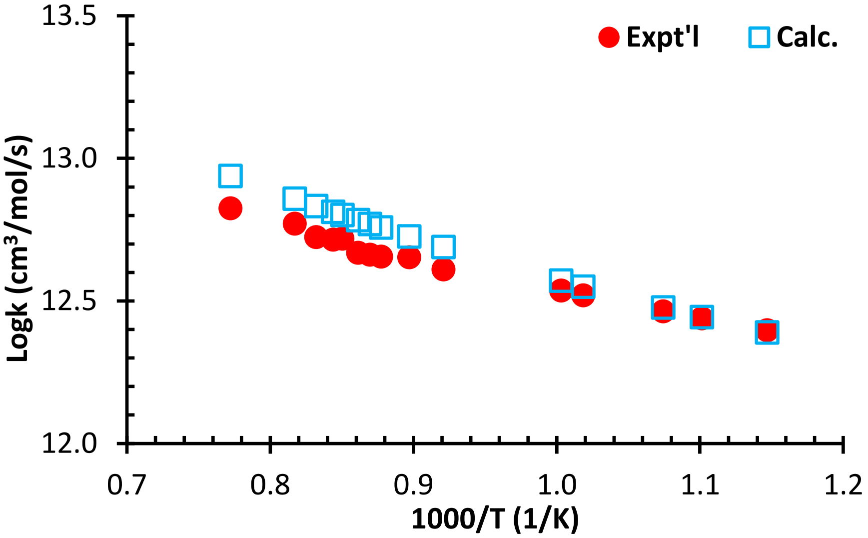


Figure S1: Comparison of the experimental and calculated rate coefficients for DMC + OH reaction. The calculations were carried out with both the deterministic and stochastic (with 10^7 numbers of trials) approaches as a function of temperature (300 – 1500 K) over the pressure range of 1.42 – 2.30 atm.

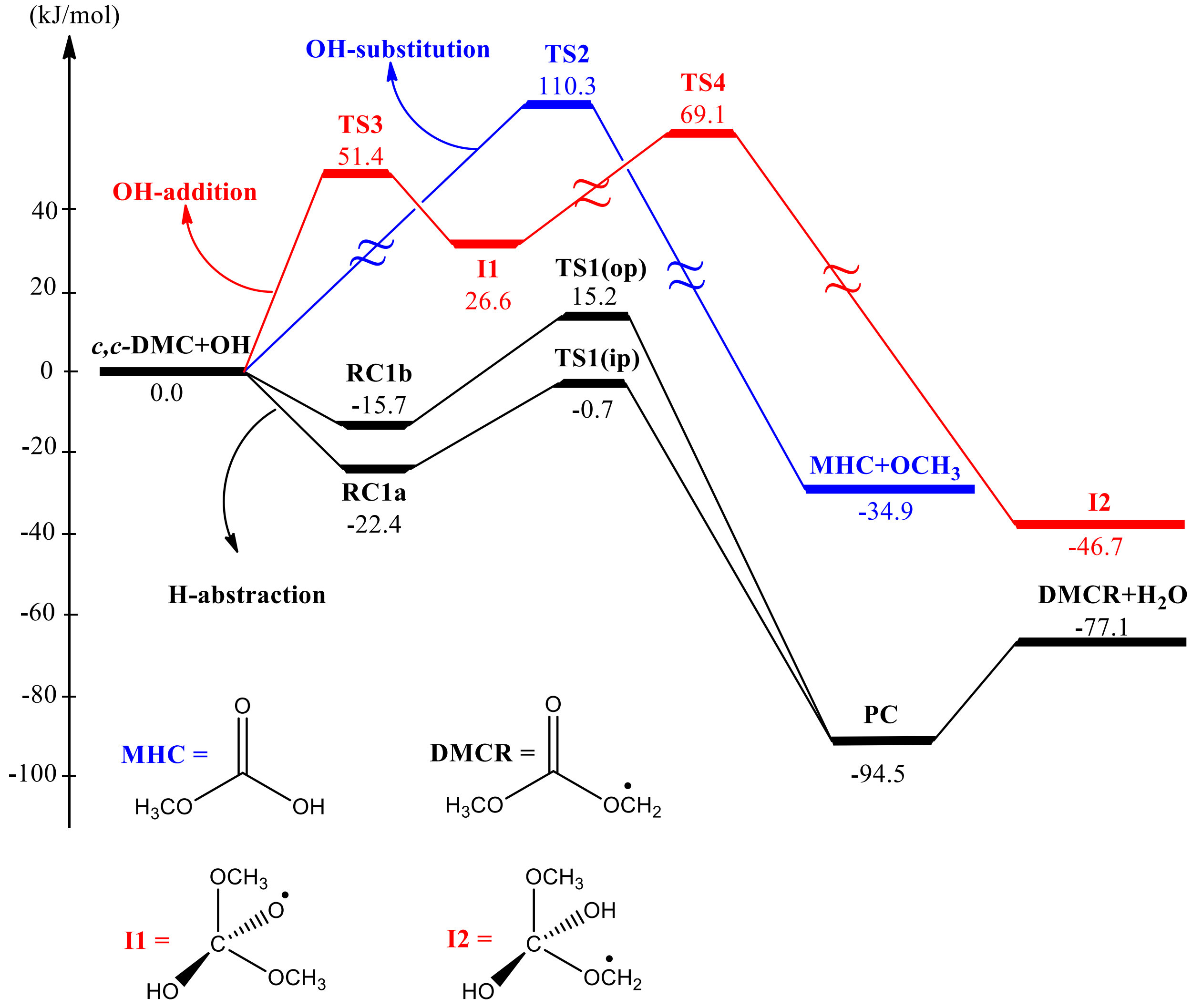
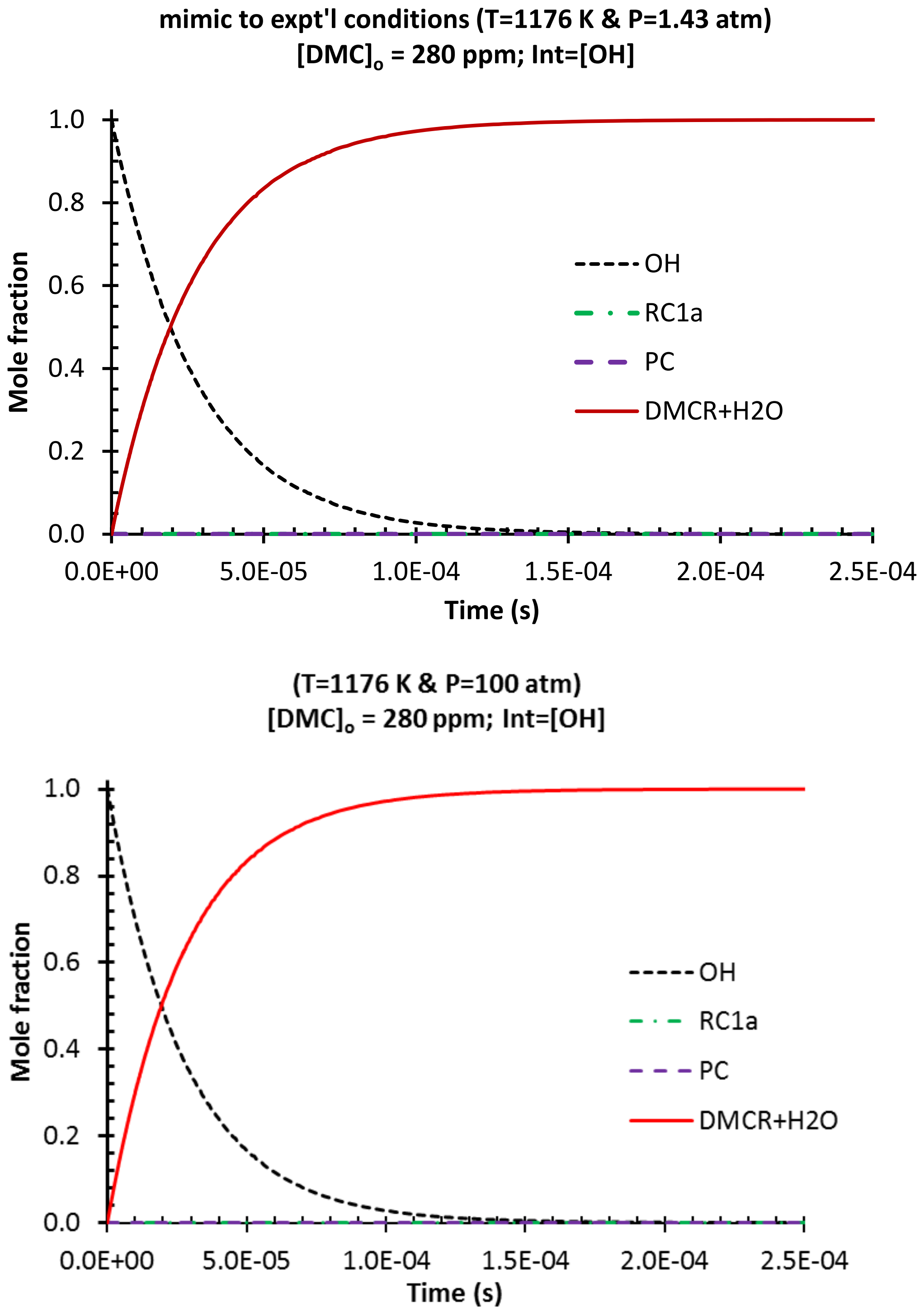


Figure S2: Zero-point corrected energies at 0 K for the simplified potential energy surface (PES) of DMC+OH reaction obtained at CCSD(T)/cc-pV(D,T)Z//MP2/aug-cc-pVDZ level of theory. Blue and Red Lines show the OH-substitution and OH-addition Channels, respectively, obtained at CBS-QB3 method. (DMC: dimethyl carbonate, DMCR: dimethyl carbonate radical, RC: hydrogen bonded pre-reaction complex, PC: post-reaction Complex, TS: transition state and MHC: methyl hydrogen carbonate). The OH-addition and/or substitution channels have no kinetic relevance due to significantly high barriers. Hence, these cannot compete with the direct H-abstraction of DMC by OH radicals.


mimic to expt'l conditions (T=1176 K & P=1.43 atm)
$[DMC]_o$ = 280 ppm; Int=[OH]

(T=1176 K & P=100 atm)
$[DMC]_o$ = 280 ppm; Int=[OH]

Figure S3: Calculated concentration time profiles for OH radicals, intermediates and products.

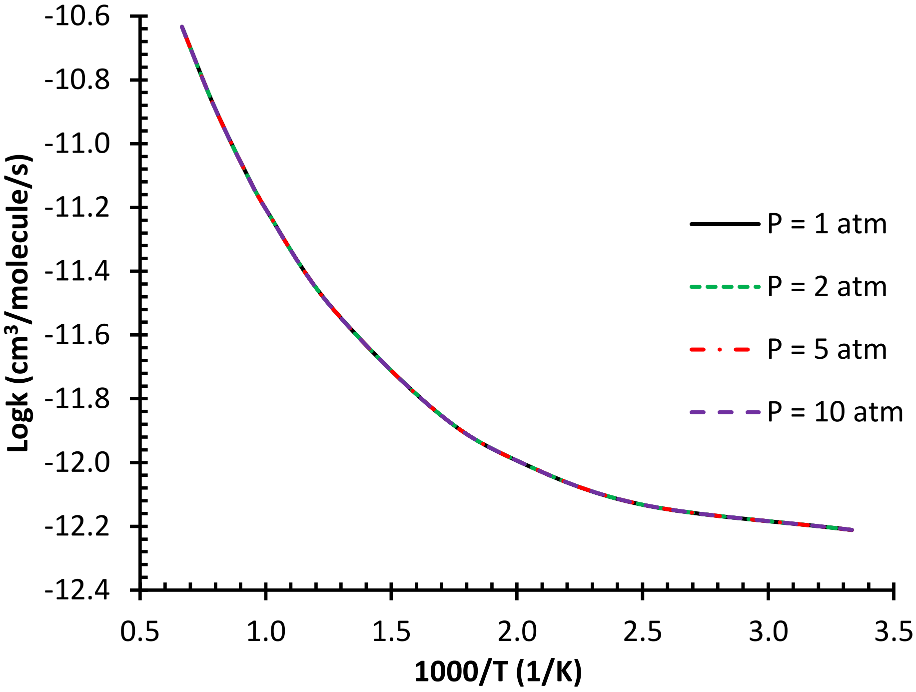


Figure S4: Calculated rate coefficients with stochastic approaches (with 10^7 numbers of trials) as a function of temperature at different pressures (p = 1, 2, 5 and 10 atm) having $k_{fitting}^{calc.}(T) = 6.59 \times 10^{-26} \left(\frac{T}{K}\right)^{4.47} exp\left(\frac{1316}{T}\right)$ (cm^3 molecule^{-1} s^{-1}) for T = 300 – 1500 K and P-independence.

Table S1: Energies, optimized geometries and vibrational frequencies of all species calculated at CCSD(T)/cc-pV(D,T)Z//MP2/aug-cc-pVDZ level of theory.

Species	Energy (Hartree)	Cartesian coordinates (in Å)				Frequencies (cm^{-1})		
***c,c*-DMC** (C$_{2v}$)	-343.28928434	6	0.248260	0.823196	1.217622	123.3	145.5	173.3
		6	2.185986	1.453822	2.353669	206.9	242.0	355.5
		1	1.759605	1.193853	3.331977	513.3	687.8	792.8
		1	3.252858	1.209050	2.314229	918.2	998.9	1135.6
		1	2.020336	2.520544	2.150843	1171.9	1175.9	1199.5
		6	-1.628132	0.125346	0.019611	1222.2	1302.5	1449.5
		1	-1.903120	1.153985	-0.250126	1473.6	1481.6	1482.2
		1	-1.841485	-0.565335	-0.803266	1490.3	1491.8	1777.2
		1	-2.163817	-0.172694	0.931030	3092.6	3093.2	3193.3
		8	-0.197579	0.027309	0.225245	3193.8	3225.7	3225.9
		8	1.581183	0.646860	1.313762			
		8	-0.432065	1.568810	1.904969			
***c,t*-DMC** (C$_s$) (not shown in PES and implicitly treated in the HIR treatment)	-343.28424556	6	0.639007	0.499004	1.141754	125.0	158.7	179.7
		6	2.757491	-0.026396	0.146327	224.1	249.2	353.4
		1	2.371984	-0.038150	-0.881801	572.1	633.5	779.7
		1	3.752408	0.431693	0.177576	860.8	1045.7	1109.8
		1	2.792355	-1.048540	0.546091	1168.1	1174.9	1187.7
		6	-1.085424	-0.988489	0.596801	1205.7	1278.7	1450.3
		1	-1.729763	-0.178937	0.229217	1475.2	1479.7	1488.4
		1	-1.206712	-1.893837	-0.008226	1490.1	1493.1	1801.5
		1	-1.310582	-1.186636	1.653072	3092.3	3095.6	3194.6
		8	0.309030	-0.621483	0.446012	3198.8	3219.9	3224.9
		8	1.939144	0.822347	0.987834			
		8	-0.123048	1.151193	1.827584			
***t,t*-DMC** (C$_2$) (not shown in PES and implicitly treated in the HIR treatment)	-343.26339268	6	0.679088	0.483036	1.118423	66.6	177.3	177.8
		6	2.982802	0.351958	0.394979	191.6	292.8	327.4
		1	2.514697	0.394822	-0.598020	544.7	639.4	792.5
		1	3.713633	1.163832	0.495844	793.1	1034.2	1106.7
		1	3.483088	-0.615508	0.539503	1129.3	1169.3	1171.9
		6	0.998631	-1.769984	0.300230	1213.1	1244.7	1458.8
		1	1.537196	-1.876901	1.251821	1477.8	1484.6	1489.6
		1	0.206736	-2.526362	0.235244	1510.4	1518.0	1806.3
		1	1.690817	-1.886274	-0.545065	3081.5	3085.0	3186.3
		8	0.329342	-0.487698	0.222947	3187.8	3202.2	3203.4
		8	2.004022	0.567495	1.440798			
		8	-0.141212	1.228539	1.600492			
OH (C$_1$)	-75.67845564	8	0.000000	0.000000	-0.007586	3767.8		
		1	0.000000	0.000000	0.967586	(3737.8[a])		

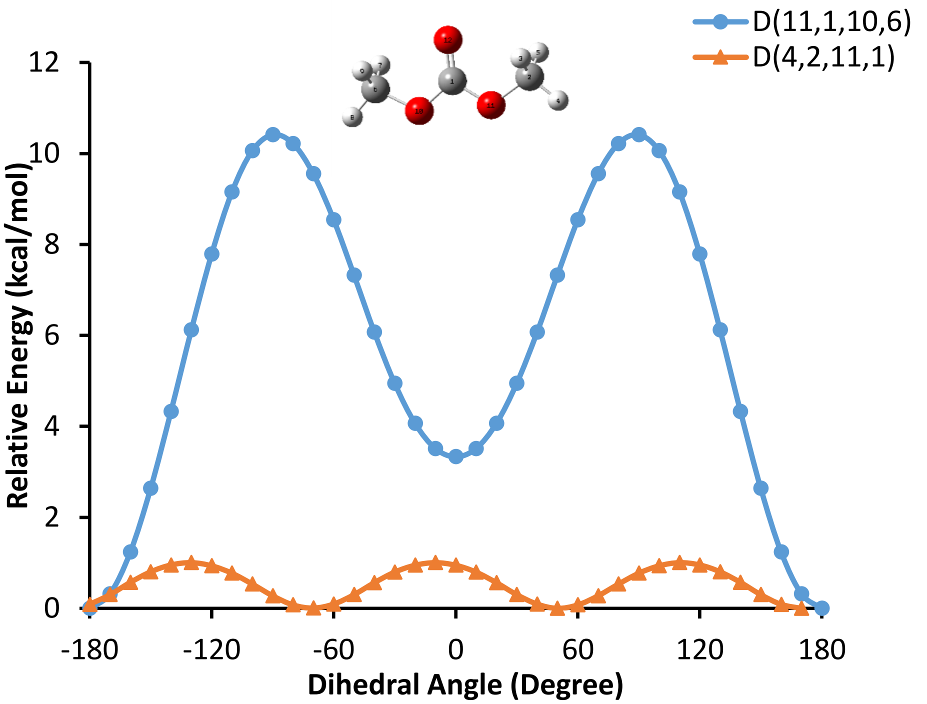
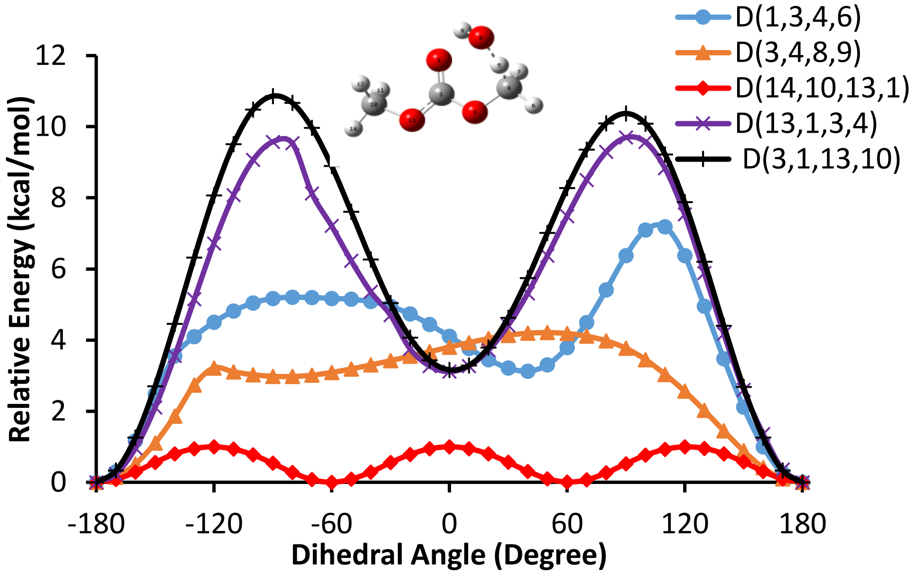
Species	Energy (Hartree)	Cartesian coordinates (in Å)				Frequencies (cm^{-1})		
RC1a (C_1)	-418.97880624	6	-0.455832	0.321381	0.227190	25.3	63.4	125.3
		8	0.298250	-0.590562	0.552330	146.9	152.9	186.6
		8	-0.117995	1.604487	0.042238	208.0	249.6	362.6
		6	1.291300	1.877500	0.263416	423.4	515.1	546.3
		1	1.905296	1.294267	-0.435136	691.9	795.9	927.7
		1	1.398363	2.950511	0.074683	990.4	1136.3	1155.6
		1	1.567976	1.632547	1.297121	1174.0	1201.0	1226.6
		8	3.074015	-1.028382	1.182602	1328.4	1450.6	1480.5
		1	2.121251	-0.916270	0.973527	1481.8	1483.7	1488.0
		6	-2.259272	-1.161171	0.165536	1490.2	1757.0	3096.3
		1	-2.088171	-1.497358	1.196724	3098.0	3199.2	3200.0
		1	-1.750533	-1.835951	-0.535535	3231.3	3232.5	3633.6
		8	-1.770638	0.194725	-0.004251			
		1	-3.330015	-1.100501	-0.055022			
RC1b (C_1)	-418.97575180	6	0.097739	0.812124	1.172869	22.2	23.7	120.3
		6	2.175357	1.268348	2.136039	131.6	141.7	169.4
		1	1.816987	1.028254	3.145851	202.5	241.1	348.3
		1	3.209152	0.935898	1.996398	359.2	468.6	520.4
		1	2.080044	2.346995	1.953750	690.3	787.9	917.8
		6	-1.926857	0.258174	0.113245	990.6	1132.9	1172.6
		1	-2.143550	1.306423	-0.130154	1176.9	1201.5	1222.9
		1	-2.245262	-0.408894	-0.695026	1293.3	1450.5	1472.4
		1	-2.406807	-0.013041	1.062517	1481.8	1482.7	1489.9
		8	-0.491219	0.060460	0.211397	1491.9	1791.0	3095.9
		8	1.411876	0.528104	1.148682	3097.7	3198.6	3203.2
		8	-0.470061	1.594916	1.913493	3230.0	3231.4	3681.1
		8	0.601980	-1.881871	-1.693883			
		1	0.416776	-1.216369	-0.999440			
TS1(ip) (C_1)	-418.96614999	6	-0.889890	-0.195698	0.192488	-2014.2	65.4	109.6
		8	-0.307214	-1.087331	0.793504	144.9	167.1	217.9
		8	-0.351737	0.984703	-0.187064	237.1	344.8	353.4
		6	1.011405	1.145844	0.200240	399.3	515.7	678.4
		1	1.689567	0.319185	-0.352539	769.0	791.8	911.4
		1	1.334579	2.122640	-0.173427	933.3	1013.5	1123.8
		1	1.155548	1.007667	1.279124	1154.2	1173.4	1206.5
		8	2.217212	-0.814853	-0.759966	1231.8	1307.5	1345.8
		1	1.651993	-1.384227	-0.201435	1453.5	1464.8	1480.5
		6	-2.861002	-1.440219	0.125117	1482.8	1489.8	1770.8
		1	-2.863877	-1.589946	1.212869	3096.1	3133.8	3199.0
		1	-2.370575	-2.290308	-0.367306	3231.7	3246.8	3714.0
		8	-2.169522	-0.207712	-0.206186			

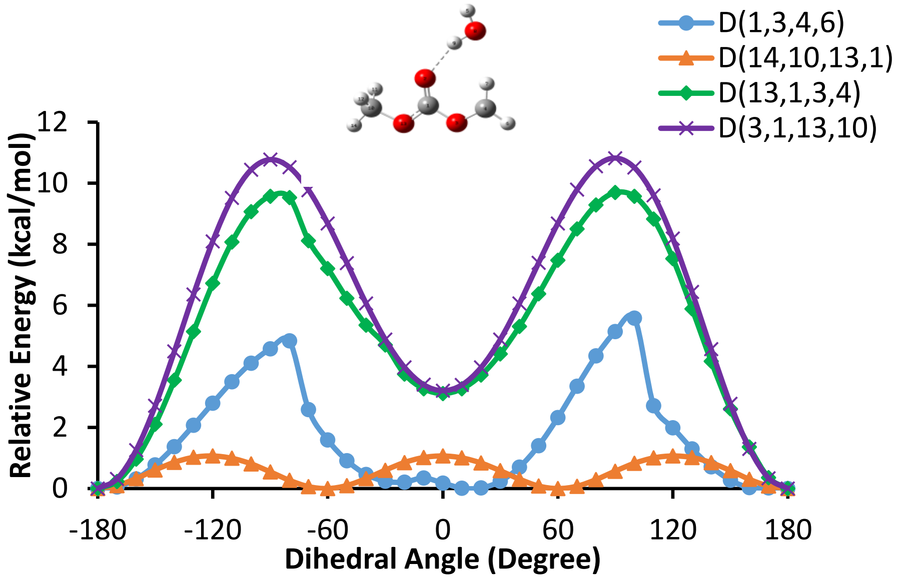
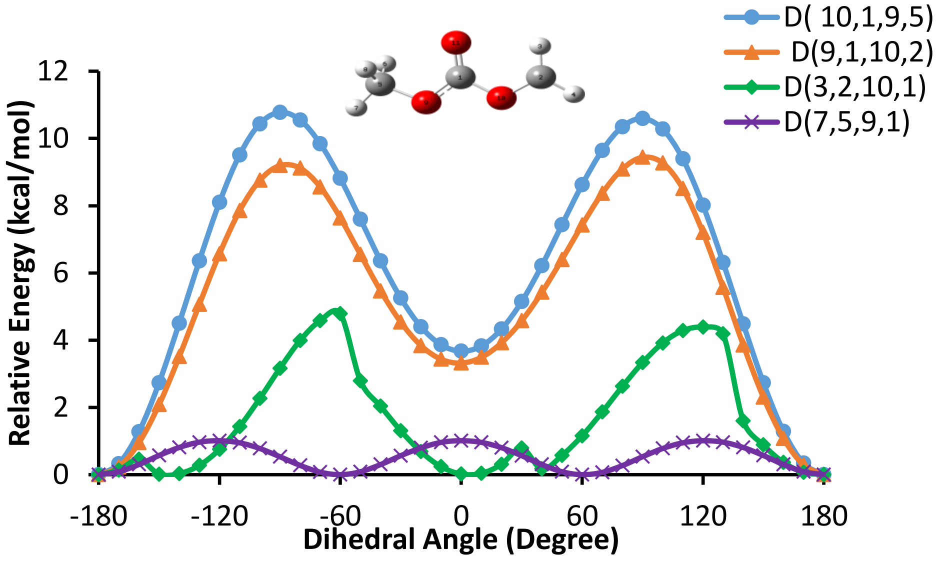
Species	**Energy (Hartree)**	**Cartesian coordinates (in Å)**				**Frequencies (cm^{-1})**		
		1	-3.877992	-1.299701	-0.255290			
TS1(op) (C_1)	-418.95901218	6	0.295765	0.857579	1.267615	-2042.0	34.4	79.4
		6	2.314611	1.390130	2.305667	120.9	152.1	178.4
		1	1.925278	1.145460	3.302885	199.6	208.5	327.3
		1	3.364059	1.092680	2.209986	328.7	504.9	648.6
		1	2.190271	2.463726	2.111204	764.8	785.1	880.4
		6	-1.655283	0.246394	0.157656	945.3	1012.1	1139.5
		1	-1.925575	1.259470	-0.165473	1144.1	1173.7	1210.0
		1	-1.947403	-0.504492	-0.737964	1226.4	1258.1	1302.6
		1	-2.196294	-0.087282	1.051949	1459.5	1476.3	1482.3
		8	-0.238743	0.082113	0.290919	1490.5	1511.2	1782.2
		8	1.617247	0.616710	1.295020	3095.4	3122.6	3198.0
		8	-0.323698	1.627447	1.981510	3226.6	3230.4	3754.0
		8	-1.888552	-1.382487	-1.695986			
		1	-0.926765	-1.539552	-1.655745			
PC (C_1)	-419.00449519	6	-0.477930	0.122977	0.197238	20.3	57.1	80.8
		8	0.117502	-0.732210	0.834195	125.4	139.8	158.4
		8	0.002600	1.328464	-0.189980	191.4	245.6	260.0
		6	1.326550	1.609302	0.145634	334.5	374.3	476.1
		1	2.807059	-1.410726	2.899336	524.1	568.2	682.2
		1	1.589738	2.628633	-0.119046	780.7	919.5	1029.4
		1	1.789953	1.042833	0.950089	1170.5	1174.1	1200.1
		8	2.477351	-0.604013	2.485785	1235.0	1311.7	1456.2
		1	1.693543	-0.883785	1.984342	1474.3	1483.2	1489.6
		6	-2.388673	-1.211473	0.101386	1636.1	1778.6	3095.9
		1	-2.435704	-1.317065	1.193388	3198.7	3222.3	3232.0
		1	-1.838782	-2.056992	-0.332655	3391.2	3729.5	3909.9
		8	-1.738588	0.037464	-0.249689			
		1	-3.392276	-1.133380	-0.329052			
c,c-DMCR (C_1)	-343.28928434	6	0.257244	0.733466	1.257706	123.0	154.1	191.2
		6	2.258855	1.173347	2.362857	251.2	259.1	371.3
		1	1.696875	1.883919	2.964305	521.3	536.5	678.7
		1	3.337458	1.180847	2.240077	778.7	909.5	1034.1
		6	-1.621732	0.149449	0.010196	1174.2	1179.8	1199.6
		1	-1.952878	1.193048	-0.075433	1232.1	1288.5	1446.3
		1	-1.828157	-0.404927	-0.911237	1465.2	1482.2	1490.1
		1	-2.108177	-0.325108	0.872850	1793.8	3095.1	3197.4
		8	-0.179898	0.095196	0.159828	3219.7	3230.1	3387.9
		8	1.616118	0.607476	1.269691			
		8	-0.419504	1.316412	2.083494			

Species	**Energy (Hartree)**	**Cartesian coordinates (in Å)**	**Frequencies (cm^{-1})**
H_2O (C_{2v})	-76.37920174	8 -0.022465 0.000000 -0.015885 1 0.024704 0.000000 0.948891 1 0.902858 0.000000 -0.293005	1622.3 3803.3 3937.5 (1595.0[b]; 3657.0[b]; 3756.0[a])

[a] From the work of Huber *et al.*[1] and [b] from the work of Shimanouchi[2].

Table S2: Torsional energy barrier for internal rotations in *c,c*-DMC, TS1(ip), PC and DMCR obtained at MP2/6-31G(d) level of theory (see main text for detailed description).

Species	Potential energy surfaces for the internal rotations	HinFreq (cm^{-1})[b]
***c,c*-DMC**[a]		123.3 (1)[c] 173.3 (3)[c]
TS1(ip)		109.6 (1)[c] 399.3 (1)[c] 167.0 (3)[c] 65.4 (1)[c] 144.8 (1)[c]

Species	Potential energy surfaces for the internal rotations	HinFreq (cm^{-1})[b]
PC		245.6 (2)[c] 158.4 (3)[c] 191.3 (1)[c] 125.3 (1)[c]
DMCR		191.2 (1)[c] 123 (1)[c] 259.1 (2)[c] 154.1 (3)[c]

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[a] Potential energy surface of *c,c*-DMC for HIRs of D(10,1,11,2) and D(1,10,6,8) are the same as D(11,1,10,6) and D(4,2,11,1), respectively, with HinFreq = 206.8 (1)[c] and 145.5 (3)[c], respectively; [b] HinFreq stands for the frequency modes of corresponding internal rotations and [c] HinSym stands for internal symmetry numbers (in parentheses) of the rotors.

References

1. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold Co, 1979.

2. T. Shimanouchi, *Tables of Molecular Vibrational Frequencies, Consolidated Volume 1, NSRDS NBS-39*.