Supplementary Information

Geometrical structures of Van der Waals complexes optimized at the CAM-B3LYP/aug-cc-pvdz level.

PO-CO2

C	1.443255	0.141550	-0.375852
C	1.135766	0.992129	0.776503
O	0.501822	-0.285021	0.619413
H	0.967601	0.407819	-1.324499
H	0.472235	1.850314	0.655097
H	1.846263	1.048104	1.603961
C	2.712757	-0.651881	-0.477621
H	3.110993	-0.870758	0.520317
H	2.532198	-1.602241	-0.996432
H	3.467192	-0.090850	-1.045688
C	-2.193011	-0.064821	-0.169951
O	-2.530739	-1.045593	0.351246
O	-1.897098	0.924758	-0.707920

ClO-CO2

C	1.442335	0.143658	-0.397711
C	1.143090	0.994386	0.753090
O	0.521839	-0.292894	0.606420
H	0.982826	0.390635	-1.357693
H	0.468621	1.842305	0.627888
H	1.863808	1.063212	1.570007
C	2.709026	-0.657762	-0.466985
H	3.089956	-0.869665	0.535676
H	2.558443	-1.593932	-1.012579
Cl	3.975656	0.267996	-1.355640
C	-2.223814	-0.060951	-0.143445
O	-2.555092	-1.069242	0.326767
O	-1.925315	0.955321	-0.627209

CO-CO2

C	-1.086622	-0.619442	-0.429225
C	-0.972793	0.841268	-0.304588
C	0.124660	-1.504889	-0.291088
O	-1.518287	0.046251	0.766065
H	-1.911575	-1.019409	-1.025449
H	-1.731185	1.451757	-0.801014
H	-0.163557	-2.430747	0.226189
H	0.443936	-1.793697	-1.304561
C	1.274719	-0.809053	0.438619
H	2.173717	-1.436497	0.383067
H	1.022124	-0.700538	1.501965
C	1.551629	0.564235	-0.170370
H	2.437848	1.017800	0.292418
H	1.785717	0.436492	-1.238584
C	0.355217	1.510814	-0.025462
H	0.314012	1.921280	0.993590
H	0.468960	2.366192	-0.704808
C	-4.300624	0.283993	1.021427
O	-4.296692	0.190733	2.178710
O	-4.353233	0.382273	-0.137708

SO-CO2

C	1.479507	0.208774	-0.317058
C	1.112560	1.125116	0.773229
O	0.549775	-0.187262	0.698952
H	1.013409	0.387841	-1.289210
H	0.411903	1.939426	0.578763
H	1.817819	1.275243	1.592832
C	2.789209	-0.499430	-0.355634
C	3.255801	-1.214255	0.749260
C	3.568267	-0.443123	-1.512158
C	4.491679	-1.851228	0.699095
H	2.633563	-1.284033	1.640345
C	4.807517	-1.075951	-1.559801
H	3.202132	0.099361	-2.384670
C	5.272982	-1.780883	-0.452931
H	4.846029	-2.412099	1.563652
H	5.408312	-1.024029	-2.467399
H	6.239770	-2.282012	-0.490151
C	-2.139202	-0.183570	-0.198016
O	-2.480788	-1.065600	0.474752
O	-1.834948	0.704603	-0.887178

Geometrical structures of Van der Waals complexes optimized at the CAM-B3LYP/6-31G(d,p) level.

PO-CO2

C	1.425781	0.136271	-0.374290
C	1.121942	0.979552	0.782700
O	0.502369	-0.296407	0.625334
H	0.949520	0.403128	-1.318719
H	0.459750	1.835708	0.667876
H	1.840795	1.047401	1.597652
C	2.703376	-0.645758	-0.481210
H	3.107170	-0.854615	0.512005
H	2.530280	-1.599428	-0.987140
H	3.450248	-0.088782	-1.054345
C	-2.156332	-0.057969	-0.173551
O	-2.514446	-1.026418	0.361400
O	-1.851218	0.920826	-0.729137

ClO-CO2

C	1.422407	0.138565	-0.392056
C	1.129185	0.979951	0.765767
O	0.525991	-0.308140	0.619613
H	0.956796	0.385770	-1.345266
H	0.452324	1.823257	0.651422
H	1.860625	1.061383	1.567420
C	2.699496	-0.647670	-0.473800
H	3.083067	-0.857690	0.524216
H	2.552143	-1.587249	-1.006338
Cl	3.953365	0.277472	-1.370093
C	-2.180859	-0.054001	-0.155167
O	-2.543840	-1.034873	0.352930
O	-1.859320	0.936292	-0.680062

CO-CO2

C	-1.094365	-0.620069	-0.421435
C	-0.979629	0.839828	-0.299994
C	0.120651	-1.504486	-0.298764
O	-1.502303	0.045714	0.774477
H	-1.922371	-1.020230	-1.008067
H	-1.741153	1.448252	-0.787826
H	-0.160584	-2.435607	0.205355
H	0.444211	-1.778792	-1.310894
C	1.262286	-0.808171	0.443736
H	2.158636	-1.434490	0.407762
H	0.990741	-0.693481	1.498053
C	1.546373	0.562953	-0.168568
H	2.429378	1.015742	0.292471
H	1.784386	0.430020	-1.231591
C	0.350617	1.512730	-0.032781
H	0.309916	1.928628	0.980186
H	0.466925	2.361147	-0.714550
C	-4.261993	0.281042	1.014336
O	-4.270941	0.175492	2.172532
O	-4.312808	0.392596	-0.145245

SO-CO2

C	1.462011	0.180157	-0.329323
C	1.115271	1.129151	0.738153
O	0.564174	-0.183950	0.717847
H	0.979724	0.327797	-1.295701
H	0.410780	1.933516	0.534299
H	1.839360	1.315735	1.528796
C	2.777722	-0.515945	-0.367929
C	3.229042	-1.244876	0.730688
C	3.575742	-0.429322	-1.506605
C	4.469702	-1.867569	0.693121
H	2.586778	-1.331567	1.600513
C	4.818689	-1.049246	-1.541803
H	3.221970	0.126707	-2.370465
C	5.269089	-1.768847	-0.440943
H	4.812177	-2.437836	1.550690
H	5.433797	-0.974650	-2.432732
H	6.237602	-2.257370	-0.469181
C	-2.103719	-0.173814	-0.154363
O	-2.451102	-1.049596	0.527010
O	-1.803512	0.708415	-0.855398

Geometrical structures of Van der Waals complexes optimized at the MP2/aug-cc-pvdz level.

PO-CO2

C	1.427425	0.141638	-0.368254
C	1.138037	0.943863	0.834454
O	0.527892	-0.372547	0.659814
H	0.899318	0.422660	-1.287732
H	0.433782	1.778489	0.771757
H	1.883470	0.987646	1.634617
C	2.725383	-0.604692	-0.534383
H	3.162411	-0.831430	0.449347
H	2.559230	-1.551410	-1.071552
H	3.440697	0.000961	-1.114459
C	-2.185461	-0.035639	-0.188043
O	-2.568051	-1.026075	0.323209
O	-1.836243	0.963879	-0.713602

ClO-CO2

Cl	3.167205	0.476390	-0.217668
C	1.775995	-0.628035	-0.543298
C	0.523074	-0.031838	0.038534
H	1.703658	-0.739976	-1.633468
H	1.997335	-1.597536	-0.078056
C	0.084542	-0.395046	1.394894
O	-0.555958	-0.992277	0.221219
H	0.203756	0.932172	-0.372997
H	-0.553913	0.295795	1.951541
H	0.691570	-1.093713	1.978511
C	-3.070905	0.373668	-0.237752
O	-3.612220	-0.547092	-0.735596
O	-2.551962	1.313386	0.256946

CO-CO2

C	0.321977	-0.639389	-0.677155
C	0.334103	0.822570	-0.434082
C	1.542346	-1.483675	-0.387451
O	-0.341247	-0.085202	0.499850
H	-0.381736	-1.024908	-1.425720
H	-0.377113	1.432907	-1.003333
H	1.216940	-2.462351	0.005301
H	2.059239	-1.673635	-1.346501
C	2.500348	-0.787338	0.591235
H	3.426615	-1.378592	0.678543
H	2.038992	-0.743431	1.591949
C	2.816649	0.631692	0.099047
H	3.606366	1.091851	0.715713
H	3.209033	0.569222	-0.932718
C	1.564184	1.525444	0.112528
H	1.335801	1.848459	1.143232
H	1.742758	2.438699	-0.479797
C	-3.150836	0.006859	0.060123
O	-2.917746	0.201725	-1.082110
O	-3.422197	-0.185923	1.190742

SO-CO2

C	-0.331043	0.394332	0.469574
C	-0.937732	-0.274058	1.643282
O	-1.203129	-0.762703	0.296985
H	-0.786163	1.336870	0.141602
H	-1.798916	0.184793	2.138749
H	-0.305906	-0.934540	2.245845
C	-3.797893	0.153943	-0.536765
O	-4.016929	-0.761811	-1.245265
O	-3.607425	1.084897	0.166465
C	1.106312	0.201911	0.125201
C	1.669489	-1.090088	0.073685
C	1.915559	1.326907	-0.135316
C	3.035174	-1.249783	-0.219809
H	1.028519	-1.960554	0.242441
C	3.282486	1.165238	-0.424377
H	1.474067	2.329173	-0.112429
C	3.845682	-0.124275	-0.465101
H	3.467409	-2.253952	-0.264390
H	3.905151	2.042308	-0.624353
H	4.907497	-0.251935	-0.695181

Geometrical structures of Van der Waals complexes optimized at the B3PW91/aug-cc-pvdz level.

PO-CO2

C	1.643072	0.161329	-0.400935
C	1.359420	1.026863	0.749858
O	0.620404	-0.185399	0.546881
H	1.238302	0.479272	-1.368410
H	0.785212	1.946949	0.611783
H	2.035410	1.013005	1.609777
C	2.842316	-0.739973	-0.460933
H	3.179343	-1.006943	0.548842
H	2.604075	-1.665317	-1.003930
H	3.667560	-0.239825	-0.988568
C	-2.423272	-0.080171	-0.138353
O	-2.666691	-1.057557	0.446726
O	-2.208603	0.901027	-0.732022

ClO-CO2

Cl	3.309188	0.248350	-0.427707
C	1.842942	-0.779105	-0.199783
C	0.642735	0.087161	0.052437
H	1.726567	-1.367321	-1.116895
H	2.032029	-1.446386	0.647484
C	0.202792	0.404528	1.412684
O	-0.473252	-0.597602	0.635585
H	0.380478	0.779647	-0.752731
H	-0.373559	1.315160	1.589553
H	0.771275	0.020694	2.263790
C	-3.316549	0.131918	-0.362120
O	-3.723481	-0.958858	-0.332423
O	-2.931331	1.232617	-0.400598

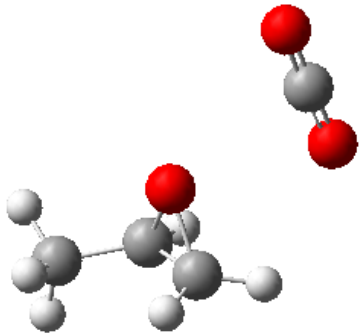
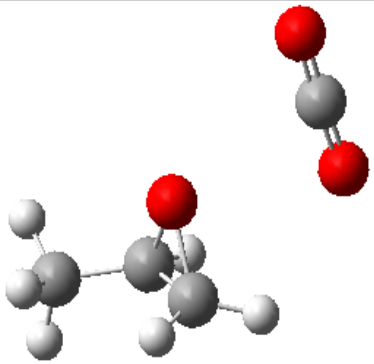
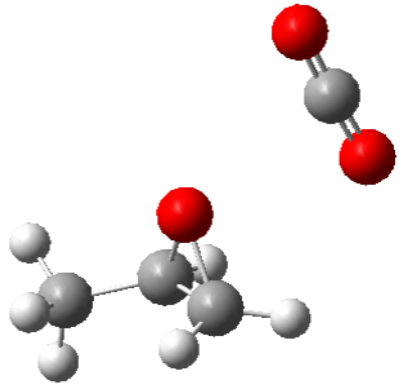
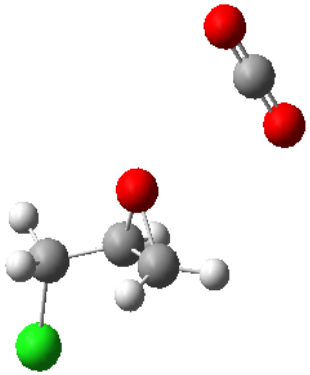
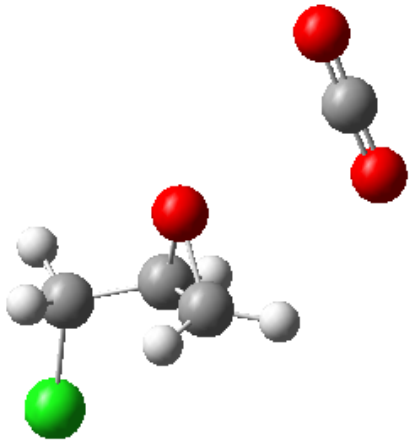
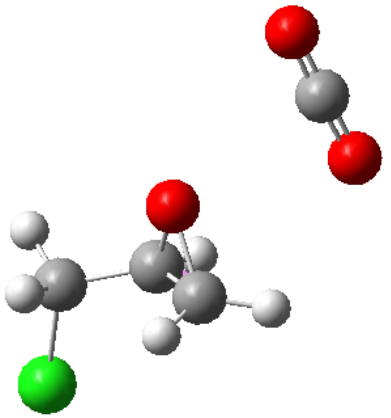
CO-CO2

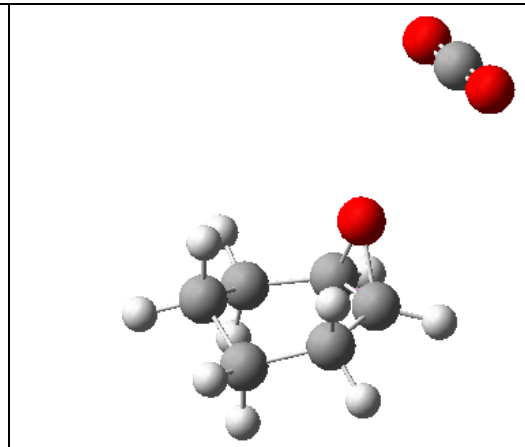
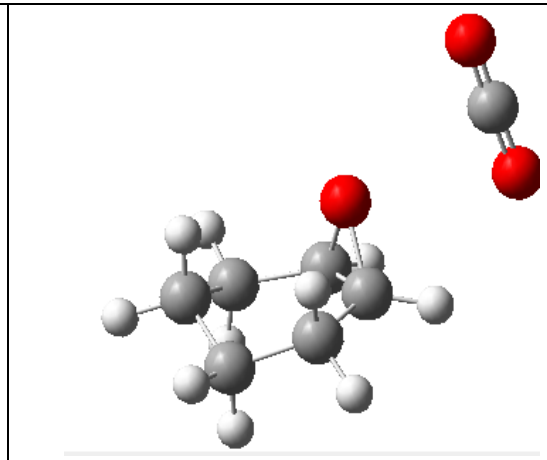
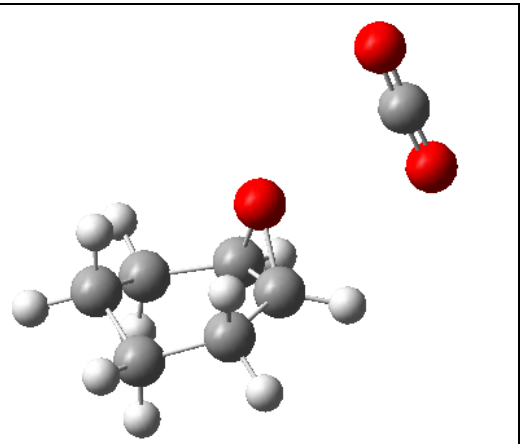
C	0.033128	0.436489	0.075835
C	0.067594	0.301716	1.543659
C	1.278396	0.231382	-0.749116
O	-0.504394	-0.729492	0.716065
H	-0.731829	1.084922	-0.365366
H	-0.686515	0.843129	2.123878
H	1.008068	-0.265086	-1.693415
H	1.667883	1.227637	-1.017262
C	2.350797	-0.564439	-0.001597
H	3.282754	-0.557348	-0.584405
H	2.035396	-1.614595	0.085337
C	2.593149	0.021328	1.389176
H	3.428269	-0.495216	1.883653
H	2.898245	1.075228	1.281291
C	1.344487	-0.054531	2.275381
H	1.224127	-1.069493	2.684374
H	1.455112	0.617368	3.138990
C	-3.055438	-2.393253	0.697660
O	-3.008144	-2.500258	1.857517
O	-3.130696	-2.303105	-0.462080

SO-CO2

C	-0.184276	0.522327	0.760322
C	-0.701834	-0.120512	1.982369
O	-1.158187	-0.529493	0.691439
H	-0.586723	1.509257	0.511864
H	-1.442452	0.399831	2.596019
H	-0.070012	-0.846624	2.500938
C	-3.941436	0.072559	-0.728685
O	-4.185151	-1.051214	-0.914643
O	-3.720042	1.204232	-0.552323
C	1.176024	0.236745	0.227039
C	1.623306	-1.077655	0.044989
C	2.030313	1.299026	-0.090823
C	2.910297	-1.321771	-0.432340
H	0.947643	-1.905789	0.260983
C	3.319985	1.053878	-0.563490
H	1.683524	2.327180	0.031659
C	3.764302	-0.258137	-0.733804
H	3.247836	-2.349285	-0.576038
H	3.976945	1.890352	-0.806062
H	4.770211	-0.451882	-1.108604

Figure S1. Optimized structure of the epoxide-CO_2 complexes at the B3LYP and MP2 level using the aug-cc-pVDZ basis set and at the CAM-B3LYP level using the 6-31G(d,p) basis set.

	B3PW91/ aug-cc-pVDZ	MP2/ aug-cc-pVDZ	CAM-B3LYP/6-31G(d,p)
PO-CO_2			
ClO-CO_2			

$CO\text{-}CO_2$			
$SO\text{-}CO_2$