Electronic Supplementary Information

for

The Criegee Intermediate-Formic Acid Reaction Explored by Rotational Spectroscopy

*Carlos Cabezas† and Yasuki Endo**

Department of Applied Chemistry, Science Building II, National Chiao Tung University, 1001 Ta-Hsueh Rd., Hsinchu 30010, Taiwan

AUTHOR INFORMATION

Corresponding Author

* endo@nctu.edu.tw

† Present Address: Instituto de Física Fundamental (IFF-CSIC), Group of Molecular Astrophysics, C/ Serrano 123, 28006 Madrid, Spain

Table of Contents

Table SI. Rotational constants and electric dipole moment components for the two lowest energy HSOZ species calculated at the CCSD/aug-cc-pVTZ level of theory. Relative energies of each conformation are also shown.

	HSOZ-1	HSOZ-2
A /MHz	6886	6768
B /MHz	3927	4001
C /MHz	3118	3160
$\|\mu_a\|$/D[a]	1.52	0.17
$\|\mu_b\|$/D	1.31	0.19
$\|\mu_c\|$/D	0.19	1.33
ΔE[a] /kcal mol^{-1}	0[b]	2.34

[a] 1 D ≈ 3.3356×10^{-30} C·m.

[b] Relative energy to that of HSOZ-1 species.

Table SII. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for HPMF-1 conformer.

O	-1.25045	0.09087	1.06774
C	-0.17597	-0.13765	1.56192
H	-0.04108	-0.44964	2.59973
O	1.00491	-0.05931	0.95712
C	1.04046	0.41224	-0.40734
H	2.10014	0.39674	-0.64424
H	0.61455	1.41146	-0.46117
O	0.39679	-0.43748	-1.29078
O	-0.88239	0.11310	-1.64379
H	-1.36329	0.01928	-0.80405

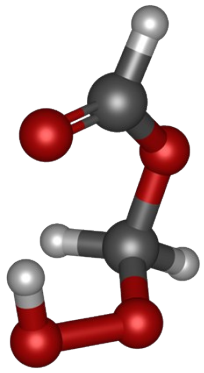

Table SIII. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for HPMF-2 conformer.

O	-0.71360	0.20655	2.01767
C	0.41102	0.30810	1.62367
H	1.21540	0.82335	2.15514
O	0.89290	-0.18675	0.46566
C	-0.04950	-0.86509	-0.36281
H	-0.81656	-1.33874	0.24416
H	0.53138	-1.57269	-0.94620
O	-0.73092	0.01859	-1.18966
O	0.19142	0.43015	-2.21327
H	0.48189	1.28399	-1.87118

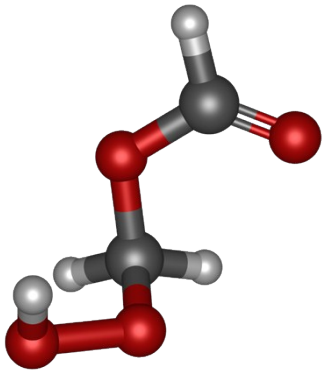

Table SIV. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for HPMF-3 conformer.

O	0.44856	-0.16433	-2.38366
C	0.11835	0.32370	-1.34879
H	0.47722	1.29074	-0.97508
O	-0.75544	-0.28452	-0.51119
C	-0.95558	0.32532	0.74244
H	-1.98591	0.14381	1.03670
H	-0.73598	1.39348	0.69036
O	-0.19251	-0.27767	1.73919
O	1.17072	0.10849	1.48351
H	1.55882	-0.74735	1.26428

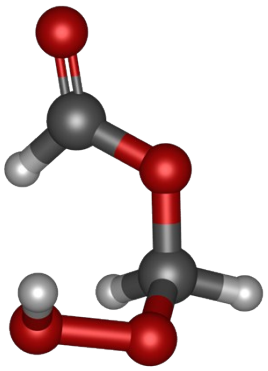

Table SV. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for HPMF-4 conformer.

O	-0.53264	0.09772	-2.48298
C	0.13946	0.27712	-1.51693
H	0.76711	1.16461	-1.35620
O	0.20861	-0.61974	-0.50478
C	0.93611	-0.20248	0.63497
H	1.80457	0.39586	0.35450
H	1.22119	-1.10890	1.16004
O	0.17982	0.63415	1.45077
O	-0.80470	-0.18794	2.09597
H	-1.53971	-0.13703	1.47153

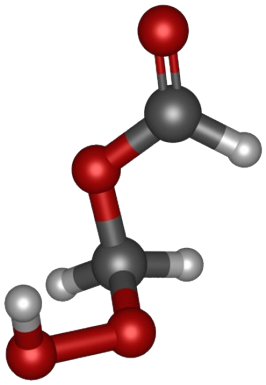

Table SVI. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for HSOZ-1 conformer.

O	-1.04999	-0.50976	0.08113
O	-0.72521	0.49649	1.06727
C	0.58501	0.08514	1.36026
H	1.09561	0.91143	1.84888
H	0.57673	-0.82219	1.96772
O	1.16125	-0.16850	0.09882
C	0.08695	-0.45791	-0.76268
H	0.17775	-1.44070	-1.21688
O	-0.00587	0.46219	-1.77262
H	-0.01413	1.33952	-1.37667

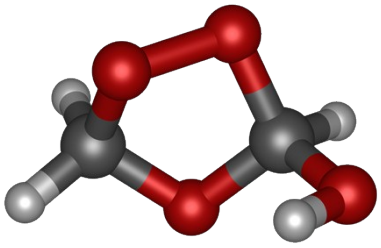

Table SVII. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for HSOZ-2 conformer.

O	-1.05084	-0.52504	0.07786
O	-0.73687	0.49428	1.05125
C	0.58624	0.12774	1.34340
H	1.08382	0.99820	1.76376
H	0.61540	-0.73698	2.00990
O	1.15937	-0.21257	0.09532
C	0.09022	-0.46760	-0.75226
H	0.16388	-1.45381	-1.21325
O	0.04532	0.55069	-1.68414
H	-0.66485	0.36130	-2.30331

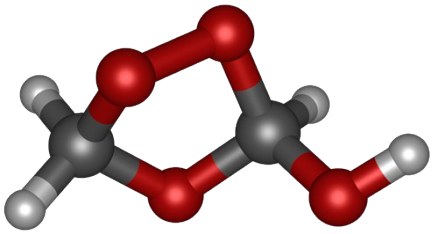

Table SVIII. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for TS-1.

O	-1.48378	1.37860	-2.41451
O	0.35007	-0.33595	-3.33790
C	2.03493	-0.72200	-1.72828
H	3.31549	-2.19879	-2.34384
H	2.32231	0.47477	-0.03862
H	-1.55477	0.40088	-0.60157
O	-1.54517	-1.27776	1.29631
C	-0.49714	-0.30283	3.25138
O	1.34974	1.14006	3.18065
H	-1.29891	-0.83655	5.09027

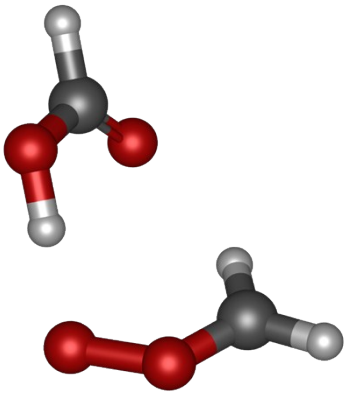

Table SIX. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for TS-2.

C	-0.88512	1.07136	-0.23304
O	-1.78122	0.20072	-0.17705
O	-1.38923	-0.86151	0.65802
H	-1.05110	1.81770	-1.00413
H	-0.07802	1.12106	0.49976
O	0.60994	-0.67632	-0.72493
H	-0.43204	-0.99382	0.18151
C	1.71468	-0.23063	-0.22481
O	1.80590	0.53690	0.72032
H	2.62061	-0.58767	-0.74095

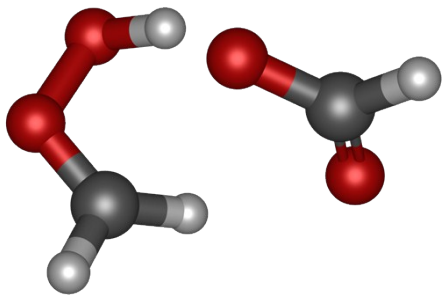

Table SX. Optimized geometry (xyz format, in Angstrom) at the CCSD/aug-cc-pVTZ level of theory for the pre-reactive complex.

O	0.04199	-1.23966	-0.95948
O	-0.30659	-0.18148	-1.77120
C	0.45341	0.80289	-1.75437
H	0.14896	1.63828	-2.36944
H	1.35059	0.77172	-1.15272
O	-0.15003	1.18158	0.86049
C	-0.43524	0.10467	1.32348
H	-1.35526	-0.43908	1.11806
O	0.32113	-0.56278	2.19772
H	1.12324	-0.04323	2.33631

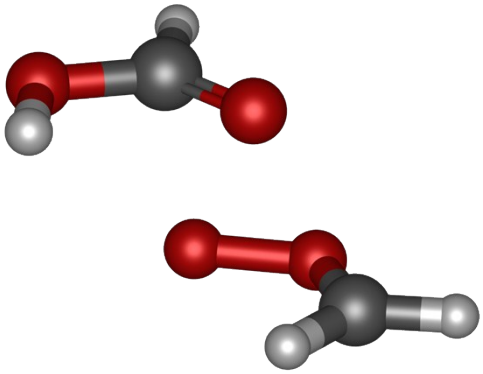

Table SXI. Observed transition frequencies for HPMF-1 species.

J′	K_a'	K_c'	J′′	K_a''	K_c''	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	1	2	1	1	1	10199.477	0.000
3	0	3	2	1	1	10985.196	0.000
2	0	2	1	0	1	10986.713	0.000
2	1	1	1	1	0	12288.417	-0.001
2	1	2	1	0	1	12793.538	0.000
3	0	3	2	1	2	14118.618	0.000
3	1	3	2	1	2	15154.153	0.000
3	0	3	2	0	2	15925.443	0.000
2	1	1	1	0	1	15926.960	0.000
3	2	2	2	2	1	16865.818	0.000
3	1	3	2	0	2	16960.977	0.000
4	1	3	3	2	2	17524.794	0.000
3	2	1	2	2	0	17806.225	-0.001
3	1	2	2	1	1	18246.445	0.001
4	0	4	3	1	3	19480.764	0.000
4	1	4	3	1	3	19984.410	0.000
2	2	1	1	1	0	20070.592	-0.001
2	2	0	1	1	0	20327.834	0.001
4	0	4	3	0	3	20516.298	-0.001
4	1	4	3	0	3	21019.945	0.000
2	2	1	1	1	1	21115.073	-0.001
2	2	0	1	1	1	21372.314	0.001
4	2	3	3	2	2	22284.553	0.000
4	3	2	3	3	1	22901.936	0.001
4	3	1	3	3	0	23137.717	-0.001
4	1	3	3	1	2	23926.343	-0.001
4	2	2	3	2	1	24250.507	0.001
5	0	5	4	1	4	24490.187	-0.001
3	2	2	2	1	1	24647.992	-0.002
5	1	5	4	1	4	24708.976	0.000
5	0	5	4	0	4	24993.834	0.000
5	1	5	4	0	4	25212.622	0.000
3	2	1	2	1	1	25845.642	0.000

Table SXII. Observed transition frequencies for $^{13}C_1$-HPMF-1 species.

J′	K_a′	K_c′	J′′	K_a′′	K_c′′	$\nu_{obs.}$	$\nu_{obs.}$-$\nu_{cal.}$
2	0	2	1	0	1	10845.833	-0.001
3	0	3	2	1	2	13874.550	0.001
3	1	3	2	1	2	14969.322	-0.002
3	0	3	2	0	2	15743.530	0.001
3	1	3	2	0	2	16838.304	0.000
3	1	2	2	1	1	17981.839	0.000

Table SXIII. Observed transition frequencies for $^{13}C_2$-HPMF-1 species.

J′	K_a′	K_c′	J′′	K_a′′	K_c′′	$\nu_{obs.}$	$\nu_{obs.}$-$\nu_{cal.}$
2	0	2	1	0	1	10937.576	-0.001
2	1	1	1	1	0	12253.437	0.002
3	0	3	2	1	2	14104.950	0.000
3	1	3	2	1	2	15080.916	0.000
3	0	3	2	0	2	15837.389	0.000
3	1	3	2	0	2	16813.354	0.000
3	1	2	2	1	1	18186.682	-0.002

Table SXIV. Observed transition frequencies for d_1-HPMF-1 species.

J′	K_a′	K_c′	J′′	K_a′′	K_c′′	F′	F′′	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	0	2	1	0	1	3	2	10601.825	0.000
						2	1	10601.825	-0.003
						1	0	10601.864	0.000
2	1	1	1	1	0	1	0	11782.995	0.002
						3	2	11783.037	-0.003
						2	1	11783.080	-0.004
2	1	2	1	0	1	2	1	12575.330	-0.002
						3	2	12575.351	0.002
						1	0	12575.395	-0.002
3	0	3	2	1	2	2	1	13454.110	-0.001
						4	3	13454.110	-0.003
						3	2	13454.137	0.004
3	1	3	2	1	2	4	3	14653.009	-0.001
						2	1	14653.009	-0.002
						3	2	14653.024	0.001
3	0	3	2	0	2	4	3	15427.636	-0.001
						3	2	15427.636	-0.002
2	1	1	1	0	1	2	1	15474.763	-0.007
						3	2	15474.785	-0.008
3	2	2	2	2	1	2	1	16224.732	0.007
						4	3	16224.755	0.004
						3	2	16224.799	0.003
3	1	3	2	0	2	3	2	16626.536	0.008
						4	3	16626.536	0.002
						2	1	16626.547	0.002
3	2	1	2	2	0	2	1	17021.877	-0.004
						4	3	17021.910	0.004
						3	2	17021.956	0.004
3	1	2	2	1	1	2	1	17521.668	-0.001
						4	3	17521.668	-0.001
						3	2	17521.682	0.001
4	0	4	3	1	3	5	4	18723.002	-0.005
						3	2	18723.002	-0.006
						4	3	18723.013	-0.002
4	1	4	3	1	3	5	4	19347.227	-0.003
						5	4	19921.901	-0.003
4	1	3	3	1	2	5	4	23035.027	0.010

Table SXV. Observed transition frequencies for d_2-HPMF-1 species.

J′	K_a′	K_c′	J′′	K_a′′	K_c′′	F′	F′′	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	1	2	1	1	1	1	0	10117.267	0.003
						3	2	10117.289	-0.001
						2	1	10117.328	0.001
2	0	2	1	0	1	3	2	10902.513	-0.001
						1	0	10902.545	0.000
2	1	1	1	1	0	1	0	12234.192	0.000
						3	2	12234.240	-0.001
						2	1	12234.281	0.003
2	1	2	1	0	1	2	1	12594.703	0.004
						3	2	12594.703	0.002
						1	0	12594.735	-0.001
3	1	3	2	1	2	4	3	15022.468	-0.002
						2	1	15022.468	-0.005
						3	2	15022.486	0.004
3	0	3	2	0	2	4	3	15772.459	0.004
						3	2	15772.461	0.000
						2	1	15772.461	-0.001
3	1	3	2	0	2	4	3	16714.657	0.000
						3	2	16714.657	-0.005
						2	1	16714.665	0.001
3	1	2	2	1	1	2	1	18151.945	-0.002
						4	3	18151.945	-0.005
						3	2	18151.966	0.004
4	1	4	3	1	3	5	4	19798.449	0.002
						4	3	19798.451	-0.002
4	0	4	3	0	3	5	4	20297.354	0.001
						5	4	20297.357	0.004

Table SXVI. Observed transition frequencies for HPMF-2 species.

J′	K_a′	K_c′	J′′	K_a′′	K_c′′	$\nu_{obs.}$	$\nu_{obs.}$-$\nu_{cal.}$
4	0	4	3	1	3	10005.133	0.000
1	1	1	0	0	0	11093.628	-0.001
1	1	0	0	0	0	11213.536	0.002
3	1	3	2	1	2	12312.555	0.000
3	0	3	2	0	2	12486.940	0.000
3	2	2	2	2	1	12494.163	0.000
3	2	1	2	2	0	12500.337	-0.002
3	1	2	2	1	1	12672.264	0.001
5	0	5	4	1	4	14380.594	0.000
2	1	2	1	0	1	15138.293	0.000
2	1	1	1	0	1	15498.011	-0.001
4	1	4	3	1	3	16414.617	-0.001
4	1	3	3	1	2	16894.177	0.001
6	0	6	5	1	5	18796.191	0.000
6	0	6	5	1	5	18796.191	0.000
3	1	3	2	0	2	19123.526	0.000
6	2	4	6	1	5	19830.870	0.000
5	2	3	5	1	4	20129.539	0.000
4	2	2	4	1	3	20393.751	0.000
3	2	1	3	1	2	20615.168	0.000
2	2	0	2	1	1	20787.093	0.000
5	0	5	4	0	4	20790.078	-0.001
2	2	1	2	1	2	21145.267	0.000
3	2	2	3	1	3	21326.876	0.000
5	2	4	5	1	5	21873.863	0.001
6	2	5	6	1	6	22240.209	0.000
4	1	4	3	0	3	23051.204	-0.001
7	0	7	6	1	6	23244.752	0.000
5	1	5	4	0	4	26924.386	0.001

Table SXVII. Observed transition frequencies for d_1-HPMF-2 species.

J′	K_a′	K_c′	J′′	K_a′′	K_c′′	F′	F′′	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
1	1	1	0	0	0	2	1	10713.247	-0.003
						1	1	10713.270	-0.004
3	1	3	2	1	2	3	2	12018.795	0.003
						4	3	12018.795	0.002
						2	1	12018.795	-0.002
3	0	3	2	0	2	2	1	12196.323	0.003
						4	3	12196.323	0.001
						3	2	12196.323	0.001
3	1	2	2	1	1	2	1	12385.584	0.002
						3	2	12385.584	0.000
						4	3	12385.584	-0.002
5	0	5	4	1	4	5	4	14187.403	-0.003
						6	5	14187.427	-0.002
2	1	2	1	0	1	3	2	14658.825	0.002
						2	1	14658.848	0.000
4	1	4	3	1	3	5	4	16022.817	-0.007
4	0	4	3	0	3	5	4	16253.661	-0.001
6	0	6	5	1	5	6	5	18508.454	0.000
						7	6	18508.478	0.003
3	1	3	2	0	2	4	3	18543.838	0.002
						3	2	18543.863	0.002

Table SXVIII. Observed transition frequencies for d_2-HPMF-2 species.

J′	K_a′	K_c′	J′′	K_a′′	K_c′′	F′	F′′	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
1	1	1	0	0	0	2	1	10788.528	-0.001
						0	1	10788.552	-0.001
3	1	3	2	1	2	3	2	12092.004	-0.003
						2	1	12092.015	0.002
						4	3	12092.026	0.002
3	0	3	2	0	2	2	1	12244.666	0.003
						3	2	12244.676	0.001
						4	3	12244.679	0.000
3	1	2	2	1	1	3	2	12406.057	0.000
						4	3	12406.075	-0.002
						2	1	12406.085	0.002
5	0	5	4	1	4	6	5	14140.510	0.001
						5	4	14140.548	0.002
2	1	2	1	0	1	1	0	14767.180	0.000
						2	1	14767.208	-0.002
						3	2	14767.230	0.007
3	1	3	2	0	2	3	2	18693.930	-0.002
						2	1	18693.967	0.000
						4	3	18693.968	-0.002
4	1	4	3	0	3	4	3	22570.153	0.003
						5	4	22570.198	-0.002