Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material

The Reaction between the Methyl Criegee Intermediate and Hydrogen Chloride: an FTMW Spectroscopic Study

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Table SI. Optimized geometries of the two conformers of CEHP.

	anti-CEHP	*syn*-CEHP
R_{H1O1}	0.9670	0.9663
R_{O1O2}	1.4311	1.4328
R_{O2C1}	1.3884	1.3932
R_{C1H2}	1.0861	1.0870
R_{C1C2}	1.5085	1.5099
R_{C2H3}	1.0887	1.0864
R_{C2H4}	1.0899	1.0905
R_{C2H5}	1.0877	1.0884
R_{C1Cl}	1.8194	1.8160
$H_1O_1O_2$	101.214	100.859
$O_1O_2C_1$	108.041	109.002
$O_2C_1H_1$	110.432	103.200
$O_2C_1C_2$	107.332	114.906
$C_1C_2H_3$	110.008	110.684
$C_1C_2H_4$	109.198	108.760
$C_1C_2H_5$	109.640	109.442
O_2C_1Cl	110.933	110.201
$H_1O_1O_2C_1$	-86.987	90.699
$O_1O_2C_1H_2$	-43.677	176.983
$O_1O_2C_1C_2$	-168.591	53.894
$O_2C_1C_2H_3$	-57.897	-65.617
$O_2C_1C_2H_4$	62.168	54.475
$O_2C_1C_2H_5$	182.136	173.917
$O_1O_2C_1Cl$	71.609	-70.837

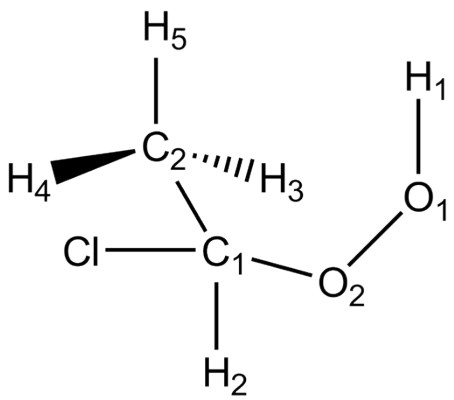

Table SII. Observed transition frequencies for the ^{35}Cl isotopic species for the conformer *anti*-CEHP.

J′	K_a′	K_c′	F′	J′′	K_a′′	K_c′′	F′′	$\nu_{obs.}$	$\nu_{obs.}$-$\nu_{cal.}$
2	0	2	2.5	1	0	1	2.5	10729.191	-2
2	0	2	2.5	1	0	1	1.5	10729.687	2
2	0	2	1.5	1	0	1	0.5	10732.004	3
2	0	2	1.5	1	0	1	2.5	10732.265	-3
2	0	2	1.5	1	0	1	1.5	10732.762	1
2	0	2	3.5	1	0	1	2.5	10733.473	1
2	0	2	0.5	1	0	1	0.5	10736.266	1
2	0	2	0.5	1	0	1	1.5	10737.022	-2
2	1	2	2.5	1	0	1	2.5	11326.545	-1
2	1	2	2.5	1	0	1	1.5	11327.041	3
2	1	2	1.5	1	0	1	0.5	11331.219	3
2	1	2	1.5	1	0	1	2.5	11331.480	-3
2	1	2	1.5	1	0	1	1.5	11331.978	2
2	1	2	3.5	1	0	1	2.5	11333.440	2
2	1	2	0.5	1	0	1	0.5	11338.100	1
2	1	1	1.5	1	1	0	1.5	12702.144	-1
2	1	1	2.5	1	1	0	1.5	12706.749	1
2	1	1	3.5	1	1	0	2.5	12707.202	4
2	1	1	0.5	1	1	0	0.5	12708.083	-1
2	1	1	2.5	1	1	0	2.5	12713.651	1
2	1	1	1.5	1	1	0	0.5	12714.548	0
3	0	3	3.5	2	1	2	3.5	14496.948	-3
3	0	3	2.5	2	1	2	1.5	14502.272	-1
3	0	3	1.5	2	1	2	0.5	14502.601	0
3	0	3	3.5	2	1	2	2.5	14503.842	0
3	0	3	4.5	2	1	2	3.5	14504.151	0
3	0	3	2.5	2	1	2	2.5	14507.209	-2
3	1	3	3.5	2	1	2	3.5	14690.483	-2
3	1	3	2.5	2	1	2	1.5	14696.165	-1
3	1	3	1.5	2	1	2	0.5	14697.259	2
3	1	3	3.5	2	1	2	2.5	14697.378	1
3	1	3	4.5	2	1	2	3.5	14698.451	1
3	1	3	2.5	2	1	2	2.5	14701.101	-2
3	0	3	3.5	2	0	2	3.5	15096.914	-3
3	0	3	3.5	2	0	2	2.5	15101.196	1
3	0	3	2.5	2	0	2	1.5	15101.487	-1
3	0	3	4.5	2	0	2	3.5	15104.118	1
3	0	3	1.5	2	0	2	0.5	15104.434	-1
3	0	3	2.5	2	0	2	2.5	15104.562	-2
3	0	3	1.5	2	0	2	1.5	15108.697	-2
3	1	3	3.5	2	0	2	3.5	15290.450	-2
3	1	3	3.5	2	0	2	2.5	15294.732	2
3	1	3	2.5	2	0	2	1.5	15295.380	0
3	1	3	4.5	2	0	2	3.5	15298.418	2
3	1	3	2.5	2	0	2	2.5	15298.452	-4
3	1	3	1.5	2	0	2	0.5	15299.091	0
3	1	3	1.5	2	0	2	1.5	15303.353	-2
2	2	1	1.5	1	1	0	1.5	16631.977	-3
2	2	1	2.5	1	1	0	1.5	16632.314	1
2	2	1	3.5	1	1	0	2.5	16638.757	2

2	2	1	2.5	1	1	0	2.5	16639.214	-1
2	2	1	0.5	1	1	0	0.5	16643.984	-3
2	2	1	1.5	1	1	0	0.5	16644.382	-2
3	2	2	3.5	2	2	1	2.5	17046.592	8
3	2	2	1.5	2	2	1	2.5	17046.592	2
3	2	2	1.5	2	2	1	1.5	17046.922	-2
3	2	2	3.5	2	2	1	3.5	17047.046	2
3	2	2	1.5	2	2	1	0.5	17047.327	7
2	2	0	1.5	1	1	0	1.5	17264.264	-5
2	2	0	2.5	1	1	0	1.5	17267.341	-1
2	2	0	3.5	1	1	0	2.5	17269.948	1
2	2	0	0.5	1	1	0	0.5	17272.423	-4
2	2	0	2.5	1	1	0	2.5	17274.242	-2
2	2	0	1.5	1	1	0	0.5	17276.671	-2
3	1	2	2.5	2	1	1	2.5	18510.798	1
3	1	2	1.5	2	1	1	1.5	18511.048	3
3	1	2	3.5	2	1	1	2.5	18512.840	4
3	1	2	4.5	2	1	1	3.5	18514.922	5
3	1	2	2.5	2	1	1	1.5	18515.404	4
3	1	2	1.5	2	1	1	0.5	18517.512	3
3	1	2	3.5	2	1	1	3.5	18519.290	2
2	2	0	0.5	1	1	1	0.5	18602.059	3
2	2	0	1.5	1	1	1	0.5	18606.305	2
2	2	0	3.5	1	1	1	2.5	18610.320	3
2	2	0	2.5	1	1	1	2.5	18614.613	1
2	2	0	1.5	1	1	1	1.5	18617.947	0
2	2	0	2.5	1	1	1	1.5	18621.024	3
3	2	1	1.5	2	2	0	1.5	18985.390	-5
3	2	1	2.5	2	2	0	2.5	18989.077	-7
3	2	1	1.5	2	2	0	0.5	18989.637	-4
3	2	1	4.5	2	2	0	3.5	18989.766	-3
3	2	1	2.5	2	2	0	1.5	18992.153	-4
3	2	1	3.5	2	2	0	2.5	18992.240	-3
4	1	4	3.5	3	1	3	2.5	19181.175	0
4	1	4	4.5	3	1	3	3.5	19181.754	1
4	1	4	2.5	3	1	3	1.5	19182.170	1
4	1	4	5.5	3	1	3	4.5	19182.750	1
4	0	4	3.5	3	0	3	2.5	19323.581	0
4	0	4	4.5	3	0	3	3.5	19323.865	1
4	0	4	2.5	3	0	3	1.5	19325.162	-1
4	0	4	5.5	3	0	3	4.5	19325.449	1
4	0	4	3.5	3	0	3	3.5	19326.948	-1
4	0	4	2.5	3	0	3	2.5	19332.371	-2

Table SIII. Observed transition frequencies for the ^{37}Cl isotopic species for the conformer *anti*-CEHP.

J′	K_a′	K_c′	F′	J′′	K_a′′	K_c′′	F′′	$\nu_{obs.}$	$\nu_{obs.}$-$\nu_{cal.}$
2	0	2	2.5	1	0	1	2.5	10552.903	-1
2	0	2	2.5	1	0	1	1.5	10554.125	2
2	0	2	1.5	1	0	1	0.5	10554.769	4
2	0	2	3.5	1	0	1	2.5	10556.745	1
2	0	2	1.5	1	0	1	1.5	10556.879	1
2	1	2	2.5	1	0	1	2.5	11153.082	1
2	1	2	2.5	1	0	1	1.5	11154.303	3
2	1	2	1.5	1	0	1	0.5	11156.076	-5
2	1	2	1.5	1	0	1	1.5	11158.199	1
2	1	2	3.5	1	0	1	2.5	11158.527	1
2	1	2	0.5	1	0	1	0.5	11161.523	1
2	1	1	1.5	1	1	0	1.5	12486.867	1
2	1	1	2.5	1	1	0	1.5	12489.907	2
2	1	1	3.5	1	1	0	2.5	12491.100	3
2	1	1	0.5	1	1	0	0.5	12492.397	-1
2	1	1	2.5	1	1	0	2.5	12495.355	1
2	1	1	1.5	1	1	0	0.5	12496.666	1
3	0	3	2.5	2	1	2	1.5	14255.266	-2
3	0	3	1.5	2	1	2	0.5	14255.751	-2
3	0	3	3.5	2	1	2	2.5	14256.399	-1
3	0	3	4.5	2	1	2	3.5	14256.871	-1
3	0	3	2.5	2	1	2	2.5	14259.163	-3
3	0	3	1.5	2	1	2	1.5	14261.187	-4
3	1	3	2.5	2	1	2	1.5	14451.823	-1
3	1	3	3.5	2	1	2	2.5	14452.724	-1
3	1	3	1.5	2	1	2	0.5	14452.802	2
3	1	3	4.5	2	1	2	3.5	14453.689	0
3	0	3	2.5	2	0	2	1.5	14856.576	-1
3	0	3	3.5	2	0	2	2.5	14856.587	1
3	0	3	4.5	2	0	2	3.5	14858.653	0
3	0	3	1.5	2	0	2	0.5	14858.681	3
3	0	3	2.5	2	0	2	2.5	14859.342	-2
3	1	3	3.5	2	0	2	3.5	15049.060	-1
3	1	3	2.5	2	0	2	1.5	15053.142	-1
3	1	3	4.5	2	0	2	3.5	15055.471	1
3	1	3	1.5	2	0	2	0.5	15055.726	0
3	1	3	2.5	2	0	2	2.5	15055.897	-2
3	1	3	1.5	2	0	2	1.5	15059.557	-1
2	2	1	1.5	1	1	0	1.5	16399.436	-3
2	2	1	2.5	1	1	0	1.5	16400.299	0
2	2	1	3.5	1	1	0	2.5	16404.551	1
2	2	1	2.5	1	1	0	2.5	16405.748	-1
2	2	1	0.5	1	1	0	0.5	16408.078	-2
2	2	1	1.5	1	1	0	0.5	16409.235	-2
3	2	2	2.5	2	2	1	2.5	16757.297	6
3	2	2	3.5	2	2	1	2.5	16757.297	3
3	2	2	2.5	2	2	1	1.5	16758.154	3
3	2	2	1.5	2	2	1	1.5	16758.154	-3
3	2	2	4.5	2	2	1	3.5	16758.492	4
3	2	2	3.5	2	2	1	3.5	16758.492	0

3	2	2	1.5	2	2	1	0.5	16759.315	1
3	1	2	2.5	2	1	1	2.5	18202.983	0
3	1	2	1.5	2	1	1	1.5	18203.417	3
3	1	2	3.5	2	1	1	2.5	18204.207	4
3	1	2	4.5	2	1	1	3.5	18205.850	5
3	1	2	2.5	2	1	1	1.5	18206.024	3
3	1	2	1.5	2	1	1	0.5	18207.684	3
3	1	2	3.5	2	1	1	3.5	18208.463	2
2	2	0	0.5	1	1	1	0.5	18331.014	0
2	2	0	1.5	1	1	1	0.5	18334.835	0
2	2	0	2.5	1	1	1	2.5	18341.044	0
2	2	0	1.5	1	1	1	1.5	18342.522	2
2	2	0	2.5	1	1	1	1.5	18345.275	1
3	2	1	2.5	2	2	0	2.5	18656.608	-6
3	2	1	4.5	2	2	0	3.5	18657.935	-4
3	2	1	1.5	2	2	0	0.5	18658.452	-5
3	2	1	3.5	2	2	0	2.5	18658.821	-3
3	2	1	2.5	2	2	0	1.5	18659.364	-4
4	1	4	3.5	3	1	3	2.5	18863.943	0
4	1	4	4.5	3	1	3	3.5	18864.414	1
4	1	4	2.5	3	1	3	1.5	18864.730	0
4	1	4	5.5	3	1	3	4.5	18865.200	1
4	0	4	3.5	3	0	3	2.5	19007.782	-1
4	0	4	4.5	3	0	3	3.5	19008.063	0
4	0	4	2.5	3	0	3	1.5	19008.944	-1
4	0	4	5.5	3	0	3	4.5	19009.229	2

Table SIV. Observed transition frequencies for the ^{35}Cl isotopic species for the conformer *syn*-CEHP.

J′	K_a′	K_c′	F′	J′′	K_a′′	K_c′′	F′′	$\nu_{obs.}$	$\nu_{obs.}$-$\nu_{cal.}$
2	1	2	2.5	1	1	1	1.5	10575.274	4
2	1	2	1.5	1	1	1	1.5	10579.363	-3
2	1	2	3.5	1	1	1	2.5	10582.605	1
2	0	2	2.5	1	0	1	2.5	11147.281	2
2	0	2	0.5	1	0	1	0.5	11154.642	1
2	0	2	2.5	1	0	1	1.5	11154.642	2
2	0	2	3.5	1	0	1	2.5	11154.961	-4
2	0	2	1.5	1	0	1	1.5	11160.138	-3
2	1	1	2.5	1	1	0	1.5	12037.129	0
2	1	1	1.5	1	1	0	1.5	12038.282	2
2	1	1	2.5	1	1	0	2.5	12042.861	0
2	1	1	1.5	1	1	0	0.5	12048.541	-2
2	1	1	0.5	1	1	0	0.5	12050.160	-3
2	1	2	1.5	1	0	1	0.5	12713.576	-3
2	1	2	2.5	1	0	1	2.5	12715.290	-1
2	1	2	0.5	1	0	1	0.5	12719.268	2
2	1	2	3.5	1	0	1	2.5	12721.003	1
2	1	2	2.5	1	0	1	1.5	12722.647	1
2	1	2	1.5	1	0	1	1.5	12726.737	-1
3	0	3	3.5	2	1	2	3.5	14806.765	-2
3	0	3	2.5	2	1	2	1.5	14812.193	-1
3	0	3	3.5	2	1	2	2.5	14812.478	1
3	0	3	1.5	2	1	2	0.5	14814.651	0
3	0	3	4.5	2	1	2	3.5	14814.913	1
3	0	3	2.5	2	1	2	2.5	14816.283	0
3	0	3	1.5	2	1	2	1.5	14820.344	-1
3	1	3	3.5	2	0	2	3.5	17340.459	-1
3	1	3	1.5	2	0	2	0.5	17346.180	1
3	1	3	2.5	2	0	2	1.5	17346.207	-1
3	1	3	4.5	2	0	2	3.5	17348.098	2
3	1	3	3.5	2	0	2	2.5	17348.140	1
3	1	3	2.5	2	0	2	2.5	17351.707	4
3	1	3	1.5	2	0	2	1.5	17353.845	-2
2	2	1	0.5	1	1	0	0.5	18461.759	2
2	2	1	3.5	1	1	0	2.5	18462.438	-6
2	2	1	2.5	1	1	0	1.5	18464.040	3
2	2	0	3.5	1	1	1	2.5	19350.152	1
2	2	0	1.5	1	1	1	1.5	19350.721	-8
2	2	0	1.5	1	1	1	0.5	19353.626	1
2	2	0	2.5	1	1	1	1.5	19356.225	-4
4	0	4	3.5	3	1	3	2.5	20386.389	1
4	0	4	4.5	3	1	3	3.5	20386.933	1
4	0	4	2.5	3	1	3	1.5	20387.378	3
4	0	4	5.5	3	1	3	4.5	20387.923	4
4	1	4	3.5	3	0	3	2.5	21867.355	-2
4	1	4	2.5	3	0	3	1.5	21867.710	3
4	1	4	4.5	3	0	3	3.5	21868.182	6
4	1	4	5.5	3	0	3	4.5	21868.535	2
4	1	4	3.5	3	0	3	3.5	21871.164	0
4	1	4	2.5	3	0	3	2.5	21875.861	-5

3	2	2	1.5	2	1	1	0.5	23386.507	3
3	2	2	4.5	2	1	1	3.5	23387.664	-5
3	2	2	3.5	2	1	1	3.5	23387.664	0
3	2	2	2.5	2	1	1	1.5	23388.118	-3
3	2	2	1.5	2	1	1	1.5	23388.118	2
3	2	2	2.5	2	1	1	2.5	23389.276	1
3	2	2	3.5	2	1	1	2.5	23389.276	1

Table SV. Observed transition frequencies for the ^{37}Cl isotopic species for the conformer *syn*-CEHP.

J´	K_a´	K_c´	F´	J´´	K_a´´	K_c´´	F´´	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	0	2	1.5	1	0	1	0.5	10909.143	1
2	0	2	0.5	1	0	1	0.5	10915.414	-3
2	0	2	2.5	1	0	1	1.5	10915.497	0
2	0	2	3.5	1	0	1	2.5	10915.723	2
2	1	2	1.5	1	0	1	0.5	12550.125	0
2	1	2	2.5	1	0	1	2.5	12551.673	4
2	1	2	0.5	1	0	1	0.5	12554.651	-2
2	1	2	3.5	1	0	1	2.5	12556.213	0
2	1	2	2.5	1	0	1	1.5	12557.731	0
2	1	2	1.5	1	0	1	1.5	12560.983	2
3	0	3	3.5	2	1	2	3.5	14403.216	0
3	0	3	2.5	2	1	2	1.5	14407.590	-3
3	0	3	3.5	2	1	2	2.5	14407.754	-2
3	0	3	1.5	2	1	2	0.5	14409.668	-1
3	0	3	4.5	2	1	2	3.5	14409.818	1
3	0	3	1.5	2	1	2	1.5	14414.189	2
3	0	3	2.5	2	0	2	1.5	16048.571	2
3	0	3	3.5	2	0	2	2.5	16049.982	1
3	0	3	4.5	2	0	2	3.5	16050.308	-5
3	1	3	3.5	2	0	2	3.5	17086.077	-2
3	1	3	1.5	2	0	2	0.5	17090.561	-2
3	1	3	2.5	2	0	2	1.5	17090.715	4
3	1	3	4.5	2	0	2	3.5	17092.190	-1
3	1	3	3.5	2	0	2	2.5	17092.355	-3
3	1	3	2.5	2	0	2	2.5	17095.208	2
3	1	3	1.5	2	0	2	1.5	17096.829	0
3	1	2	3.5	2	1	1	2.5	17540.366	1
3	1	2	4.5	2	1	1	3.5	17541.961	1
2	2	1	1.5	1	1	0	1.5	18360.118	2
2	2	1	0.5	1	1	0	0.5	18362.257	-3
2	2	1	3.5	1	1	0	2.5	18362.949	-1
2	2	1	2.5	1	1	0	1.5	18364.440	-1
2	2	1	1.5	1	1	0	0.5	18368.273	1
2	2	1	2.5	1	1	0	2.5	18368.992	2
2	2	0	3.5	1	1	1	2.5	19208.570	-4
2	2	0	1.5	1	1	1	1.5	19208.858	1
2	2	0	1.5	1	1	1	0.5	19211.556	0
2	2	0	2.5	1	1	1	1.5	19213.354	0
2	2	0	2.5	1	1	1	2.5	19214.855	2
4	1	4	3.5	3	0	3	2.5	21512.917	-4
4	1	4	2.5	3	0	3	1.5	21513.123	3

4	1	4	4.5	3	0	3	3.5	21513.615	1
4	1	4	5.5	3	0	3	4.5	21513.820	-1
3	2	2	1.5	2	1	1	0.5	23188.371	-1
3	2	2	3.5	2	1	1	3.5	23189.448	1
3	2	2	2.5	2	1	1	1.5	23189.871	1
3	2	2	1.5	2	1	1	1.5	23189.871	0
3	2	2	2.5	2	1	1	2.5	23190.946	0
3	2	2	3.5	2	1	1	2.5	23190.946	3

FTMW-MW/mmW double-resonance spectroscopy

A scheme of the arrangement of the MW/millimeter-wave radiation and the FTMW cavity is shown in Figure S1. In the experimental procedure, the FID signal of a known rotational transition is monitored with ordinary FTMW spectroscopy. The microwave or millimeter-wave radiation is guided into the center of the FTMW chamber from a horn through a Teflon window perpendicular to the directions of the microwave and the molecular beam. The standing wave of the incident microwave, the pump radiation of microwave/millimeter-wave, and the supersonic jet intersect at the center of the vacuum chamber as shown in Figure S1. Sources of the pump radiations are two synthesizers (Rohde & Schwartz, SMR-40, 1-40 GHz and Anritsu MG3692G, 1-20 GHz) and a frequency doubler (MITEQ MAX2M200400-20P). A microwave/millimeter-wave detector for each frequency region is located at the opposite side of the pump radiation source to check its power.

The frequency of the pump radiation is scanned with an appropriate frequency step and a number of accumulations at each step depending on the experimental conditions and purposes as described later. When the pump radiation is resonant to a transition, connecting the upper or lower level of the monitored microwave transition, a double-resonance spectrum is observed as a change of the intensity of the monitored microwave signal, confirming or not the identity of the observed transitions. The frequency step of a scan is set to 50-200 kHz for a spectral search in a wide frequency region, because the double-resonance signal easily saturates and is broadened when the incident power of the pump radiation is not attenuated, where the full width half maximum (FWHM) width of a double-resonance signal exceeds 200 kHz for ordinary allowed transitions. However, such a wide frequency scan does not provide accurate transition frequencies. Fine scans are performed to determine accurate transition frequencies. In the fine scans, the step size is reduced to 5-10 kHz and the power of the pump radiation is attenuated to decrease the power saturation. The FWHM of a typical double-resonance spectrum is reduced to about 40-80 kHz for ordinary transitions. The transition frequencies are obtained by Gaussian fittings of the profiles of the double-resonance spectra.

Figure S1. Experimental arrangement of the double-resonance spectrometer.