Supplementary Information: Full-dimensional Potential Energy Surface for Acetylacetone and Tunneling Splittings

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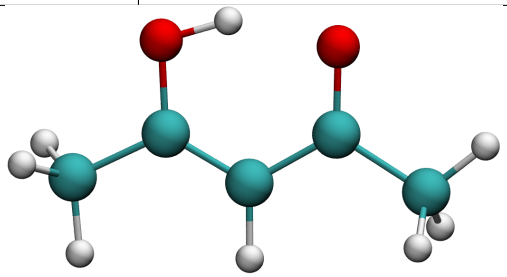
I. STATIONARY POINTS IN ACAC PES

Table S1. Coordinates, harmonic frequencies, and energy (the value in parenthesis is relative to the GM in cm^{-1}) of GM computed using MP2/aVTZ level of theory. The harmonic frequencies from the 4-(9,11,11,8) PES are shown in parenthesis.

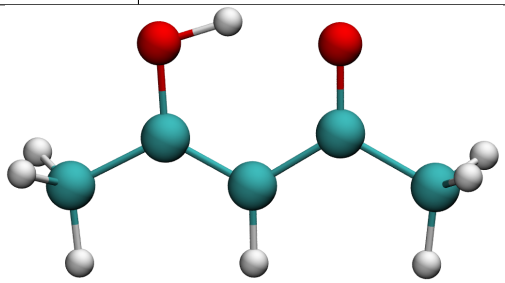
Atom	x	y	z	Mode	Freq.	Mode	Freq.	Mode	Freq.
C	0.114994	1.114431	0.419781	1	53 (97)	14	946 (936)	27	1490 (1497)
O	0.912576	1.409955	-0.598424	2	118 (119)	15	1004 (942)	28	1495 (1505)
H	0.947076	0.570389	-1.152146	3	151 (153)	16	1014 (1014)	29	1507 (1512)
O	0.518145	-0.948617	-1.417858	4	185 (189)	17	1036 (1048)	30	1658 (1655)
C	-0.220211	-1.145674	-0.429529	5	232 (229)	18	1049 (1058)	31	1697 (1704)
C	-0.881173	-2.482281	-0.238742	6	374 (364)	19	1068 (1071)	32	3013 (2855)
H	-1.964186	-2.359012	-0.211457	7	390 (390)	20	1190 (1200)	33	3074 (3095)
H	-0.605318	-3.149473	-1.049741	8	507 (507)	21	1289 (1290)	34	3079 (3099)
H	-0.577206	-2.912628	0.715851	9	555 (567)	22	1391 (1384)	35	3155 (3178)
C	-0.463523	-0.117426	0.549888	10	645 (650)	23	1394 (1399)	36	3158 (3187)
H	-1.105673	-0.314563	1.394059	11	653 (656)	24	1420 (1433)	37	3194 (3208)
C	-0.077199	2.236268	1.378546	12	794 (803)	25	1470 (1470)	38	3200 (3218)
H	0.889213	2.539729	1.780600	13	925 (921)	26	1485 (1494)	39	3250 (3258)
H	-0.498652	3.093677	0.854224						
H	-0.735725	1.948458	2.193025						



$E_{elec} = -345.17690986$ hartree (0.0 cm^{-1})

Table S2. Coordinates, harmonic frequencies, and energy (the value in parenthesis is relative to the GM in cm^{-1}) of TS(T)-I computed using MP2/aVTZ level of theory. The harmonic frequencies from the 4-(9,11,11,8) PES are shown in parenthesis.

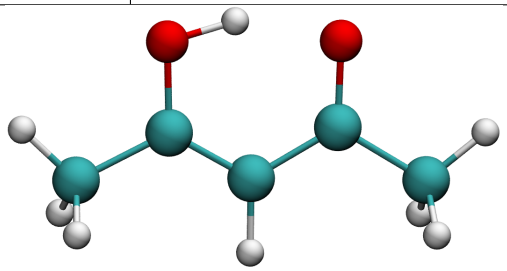
Atom	x	y	z	Mode	Freq.	Mode	Freq.	Mode	Freq.
C	-0.139141	0.000000	1.200074	1	$68i$ ($77i$)	14	945 (943)	27	1493 (1504)
O	1.182941	0.000000	1.262170	2	118 (117)	15	1026 (948)	28	1497 (1505)
H	1.485515	0.000000	0.297310	3	149 (151)	16	1026 (1028)	29	1513 (1512)
O	1.183331	0.000000	-1.248444	4	184 (190)	17	1035 (1048)	30	1651 (1649)
C	-0.068098	0.000000	-1.232146	5	238 (227)	18	1047 (1052)	31	1692 (1699)
C	-0.812086	0.000000	-2.539567	6	374 (366)	19	1069 (1070)	32	2926 (2796)
H	-0.516409	-0.878500	-3.111787	7	400 (402)	20	1190 (1197)	33	3079 (3099)
H	-1.890064	0.000000	-2.402001	8	506 (500)	21	1290 (1288)	34	3081 (3100)
H	-0.516409	0.878500	-3.111787	9	561 (568)	22	1384 (1371)	35	3159 (3187)
C	-0.804051	0.000000	0.002250	10	643 (643)	23	1395 (1398)	36	3168 (3191)
H	-1.882107	0.000000	-0.004573	11	654 (648)	24	1415 (1431)	37	3191 (3207)
C	-0.808931	0.000000	2.528931	12	792 (785)	25	1470 (1474)	38	3195 (3209)
H	-0.496668	0.879093	3.092295	13	944 (935)	26	1490 (1481)	39	3258 (3263)
H	-0.496668	-0.879093	3.092295						
H	-1.890050	0.000000	2.424226						



$E_{elec} = -345.17655832$ hartree (77.2 cm^{-1})

Table S3. Coordinates, harmonic frequencies, and energy (the value in parenthesis is relative to the GM in cm^{-1}) of TS(T)-II computed using MP2/aVTZ level of theory. The harmonic frequencies from the 4-(9,11,11,8) PES are shown in parenthesis.

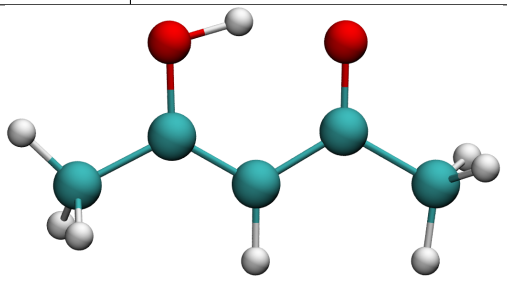
Atom	x	y	z	Mode	Freq.	Mode	Freq.	Mode	Freq.
C	0.148366	0.000000	1.205805	1	158i (140i)	14	945 (947)	27	1495 (1497)
O	-1.174224	0.000000	1.274414	2	38 (93)	15	1012 (988)	28	1500 (1499)
H	-1.481134	0.000000	0.311110	3	128 (133)	16	1030 (1012)	29	1516 (1530)
O	-1.185844	0.000000	-1.241238	4	183 (192)	17	1031 (1040)	30	1656 (1648)
C	0.065349	0.000000	-1.226882	5	233 (237)	18	1051 (1060)	31	1692 (1694)
C	0.829432	0.000000	-2.521649	6	372 (361)	19	1068 (1065)	32	2932 (2647)
H	1.472404	-0.879040	-2.572634	7	388 (394)	20	1189 (1207)	33	3074 (3095)
H	0.137032	0.000000	-3.358060	8	518 (526)	21	1296 (1298)	34	3085 (3102)
H	1.472404	0.879040	-2.572634	9	562 (573)	22	1390 (1385)	35	3156 (3178)
C	0.805378	0.000000	0.005099	10	642 (652)	23	1397 (1404)	36	3166 (3184)
H	1.884550	0.000000	-0.008603	11	657 (660)	24	1411 (1424)	37	3197 (3213)
C	0.838054	0.000000	2.531403	12	797 (809)	25	1466 (1470)	38	3200 (3217)
H	1.471438	0.880482	2.628644	13	921 (922)	26	1485 (1495)	39	3246 (3254)
H	1.471438	-0.880482	2.628644						
H	0.100270	0.000000	3.328615						



$E_{elec} = -345.17477759$ hartree (468.0 cm^{-1})

Table S4. Coordinates, harmonic frequencies, and energy (the value in parenthesis is relative to the GM in cm^{-1}) of TS(T)-III computed using MP2/aVTZ level of theory. The harmonic frequencies from the 4-(9,11,11,8) PES are shown in parenthesis.

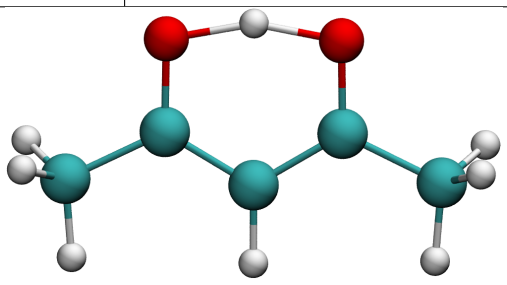
Atom	x	y	z	Mode	Freq.	Mode	Freq.	Mode	Freq.
C	0.158071	0.000000	1.181680	1	154i (136i)	14	949 (946)	27	1499 (1498)
O	-1.161280	0.000000	1.242711	2	57i (72i)	15	1025 (1004)	28	1499 (1504)
H	-1.461267	0.000000	0.270809	3	132 (135)	16	1030 (1027)	29	1522 (1532)
O	-1.176013	0.000000	-1.254083	4	181 (192)	17	1046 (1040)	30	1650 (1644)
C	0.077782	0.000000	-1.246365	5	238 (234)	18	1050 (1055)	31	1688 (1687)
C	0.809694	0.000000	-2.560251	6	370 (358)	19	1076 (1064)	32	2826 (2559)
H	0.509149	-0.878481	-3.129963	7	399 (408)	20	1188 (1204)	33	3081 (3100)
H	1.888865	0.000000	-2.431949	8	517 (518)	21	1297 (1297)	34	3085 (3102)
H	0.509149	0.878481	-3.129963	9	567 (574)	22	1380 (1365)	35	3166 (3184)
C	0.819750	0.000000	-0.020126	10	648 (648)	23	1396 (1401)	36	3167 (3191)
H	1.898203	0.000000	-0.031326	11	651 (650)	24	1408 (1422)	37	3190 (3207)
C	0.846082	0.000000	2.507677	12	794 (790)	25	1465 (1475)	38	3197 (3213)
H	1.479870	0.880341	2.604302	13	935 (936)	26	1493 (1484)	39	3254 (3260)
H	1.479870	-0.880341	2.604302						
H	0.107949	0.000000	3.304522						



$E_{elec} = -345.17454518$ hartree (519.0 cm^{-1})

Table S5. Coordinates, harmonic frequencies, and energy (the value in parenthesis is relative to the GM in cm^{-1}) of TS(H) computed using MP2/aVTZ level of theory. The harmonic frequencies from the 4-(9,11,11,8) PES are shown in parenthesis.

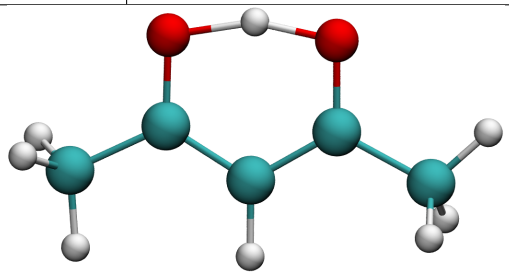
Atom	x	y	z	Mode	Freq.	Mode	Freq.	Mode	Freq.
C	-0.978305	-0.246820	-0.650513	1	1057i (921i)	14	953 (953)	27	1492 (1500)
O	-1.562772	-0.485616	0.469230	2	81 (53)	15	986 (979)	28	1495 (1502)
H	-0.676907	-0.273955	1.253628	3	88 (57)	16	1032 (1039)	29	1565 (1567)
O	0.418453	0.022490	1.650044	4	157 (156)	17	1036 (1043)	30	1621 (1629)
C	1.033406	0.269105	0.548472	5	194 (198)	18	1052 (1060)	31	1648 (1670)
C	2.465792	0.682232	0.646379	6	282 (285)	19	1067 (1062)	32	1870 (1685)
H	2.536596	1.583343	1.254665	7	410 (417)	20	1191 (1189)	33	3080 (3098)
H	3.029286	-0.100744	1.152786	8	536 (531)	21	1295 (1223)	34	3081 (3099)
H	2.897738	0.867864	-0.333205	9	541 (539)	22	1345 (1347)	35	3164 (3190)
C	0.365195	0.147787	-0.676334	10	576 (580)	23	1401 (1409)	36	3164 (3190)
H	0.867775	0.351183	-1.607107	11	663 (645)	24	1412 (1422)	37	3192 (3207)
C	-1.793208	-0.410039	-1.891996	12	762 (740)	25	1486 (1496)	38	3192 (3208)
H	-1.214502	-0.186724	-2.784100	13	784 (756)	26	1491 (1496)	39	3269 (3282)
H	-2.164949	-1.432892	-1.943039						
H	-2.657615	0.251196	-1.841063						



$E_{elec} = -345.17343253$ hartree (763.2 cm^{-1})

Table S6. Coordinates, harmonic frequencies, and energy (the value in parenthesis is relative to the GM in cm^{-1}) of TS(HT)-I computed using MP2/aVTZ level of theory. The harmonic frequencies from the 4-(9,11,11,8) PES are shown in parenthesis.

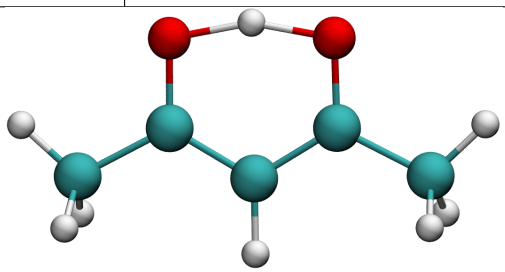
Atom	x	y	z	Mode	Freq.	Mode	Freq.	Mode	Freq.
C	0.132445	0.016302	1.140669	1	1024i (845i)	14	942 (944)	27	1492 (1500)
O	-1.155326	0.009741	1.126535	2	112i (65i)	15	983 (982)	28	1497 (1504)
H	-1.383233	0.003723	-0.028549	3	83 (42)	16	1026 (1025)	29	1567 (1569)
O	-1.161441	-0.000178	-1.237403	4	148 (149)	17	1034 (1042)	30	1623 (1630)
C	0.121709	0.006244	-1.257524	5	198 (203)	18	1055 (1061)	31	1652 (1669)
C	0.785301	0.004053	-2.597245	6	281 (285)	19	1063 (1065)	32	1872 (1692)
H	0.467412	-0.878633	-3.151120	7	408 (416)	20	1190 (1197)	33	3080 (3098)
H	1.868419	0.009989	-2.509889	8	541 (539)	21	1298 (1219)	34	3081 (3099)
H	0.458461	0.878837	-3.158388	9	543 (541)	22	1347 (1346)	35	3162 (3181)
C	0.849953	0.014956	-0.059940	10	576 (583)	23	1399 (1407)	36	3165 (3190)
H	1.927595	0.020398	-0.061417	11	659 (649)	24	1414 (1424)	37	3191 (3207)
C	0.809092	0.025288	2.474648	12	771 (752)	25	1478 (1495)	38	3199 (3215)
H	1.440286	0.908605	2.567135	13	784 (770)	26	1492 (1498)	39	3264 (3278)
H	1.449377	-0.850667	2.574363						
H	0.064661	0.024716	3.265304						



$E_{elec} = -345.17248921$ hartree (970.2 cm^{-1})

Table S7. Coordinates, harmonic frequencies, and energy (the value in parenthesis is relative to the GM in cm^{-1}) of TS(HT)-II computed using MP2/aVTZ level of theory. The harmonic frequencies from the 4-(9,11,11,8) PES are shown in parenthesis.

Atom	x	y	z	Mode	Freq.	Mode	Freq.	Mode	Freq.
C	0.129447	-0.005040	1.207402	1	1051i (865i)	14	935 (938)	27	1497 (1499)
O	-1.156174	-0.006631	1.190245	2	114i (53i)	15	979 (981)	28	1498 (1504)
H	-1.380164	-0.002151	0.008383	3	107i (48i)	16	1024 (1016)	29	1569 (1571)
O	-1.156126	0.002907	-1.173444	4	140 (144)	17	1027 (1034)	30	1626 (1628)
C	0.129497	0.004636	-1.190535	5	204 (208)	18	1057 (1065)	31	1651 (1678)
C	0.807608	0.010896	-2.524862	6	279 (285)	19	1059 (1067)	32	1870 (1679)
H	1.444494	-0.867579	-2.624466	7	404 (413)	20	1190 (1202)	33	3080 (3097)
H	0.063276	0.013126	-3.315604	8	541 (536)	21	1306 (1224)	34	3080 (3098)
H	1.442222	0.891787	-2.617366	9	549 (561)	22	1349 (1348)	35	3161 (3180)
C	0.851898	0.000731	0.008452	10	577 (586)	23	1396 (1406)	36	3161 (3181)
H	1.930043	0.002122	0.008479	11	653 (653)	24	1417 (1427)	37	3199 (3215)
C	0.807507	-0.009549	2.541763	12	772 (752)	25	1479 (1498)	38	3199 (3216)
H	1.442118	0.870566	2.641397	13	784 (784)	26	1479 (1498)	39	3259 (3275)
H	1.444389	-0.888799	2.634298						
H	0.063145	-0.013701	3.332468						



$E_{elec} = -345.17157419$ hartree (1171.0 cm^{-1})

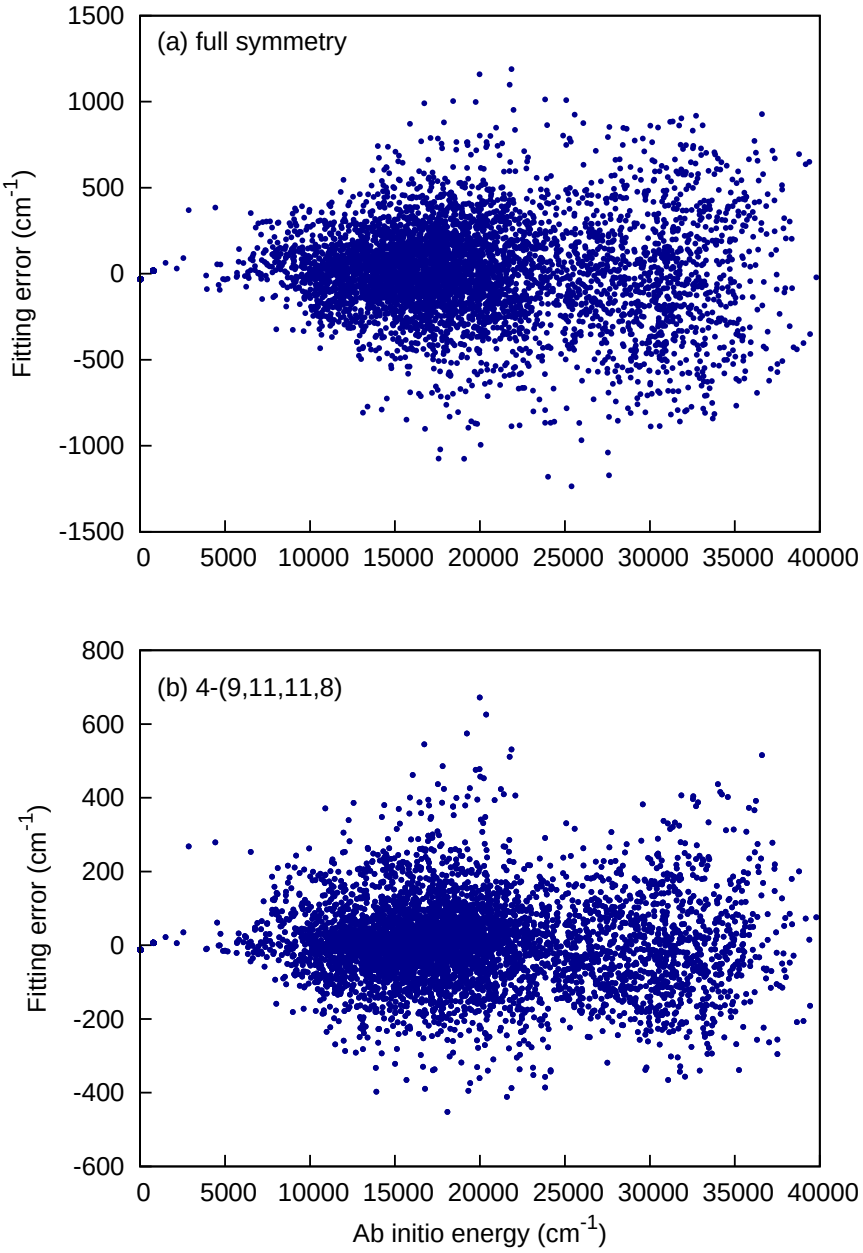


Fig. S1: Fitting errors vs. *ab initio* energies for (a) full symmetry PES and (b) 4-(9,11,11,8) PES. Only 5450 points are shown in the plots; the remaining 4 are off-scale because they were added to fix holes and therefore they have extremely high energies.