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

Supporting Information

Diagram for comprehensive molecular orbital-based chemical reaction analyses: reactive orbital energy diagram

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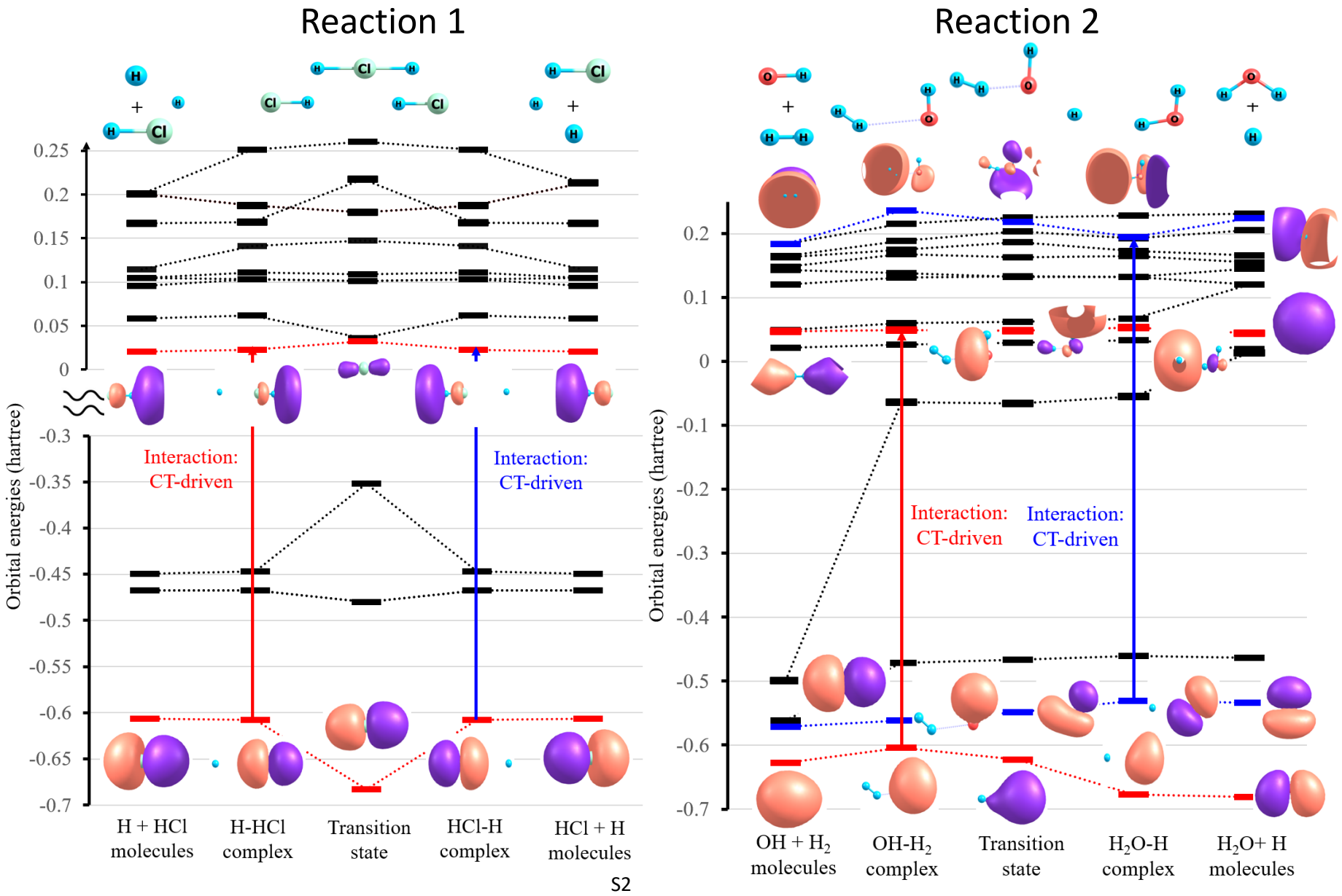
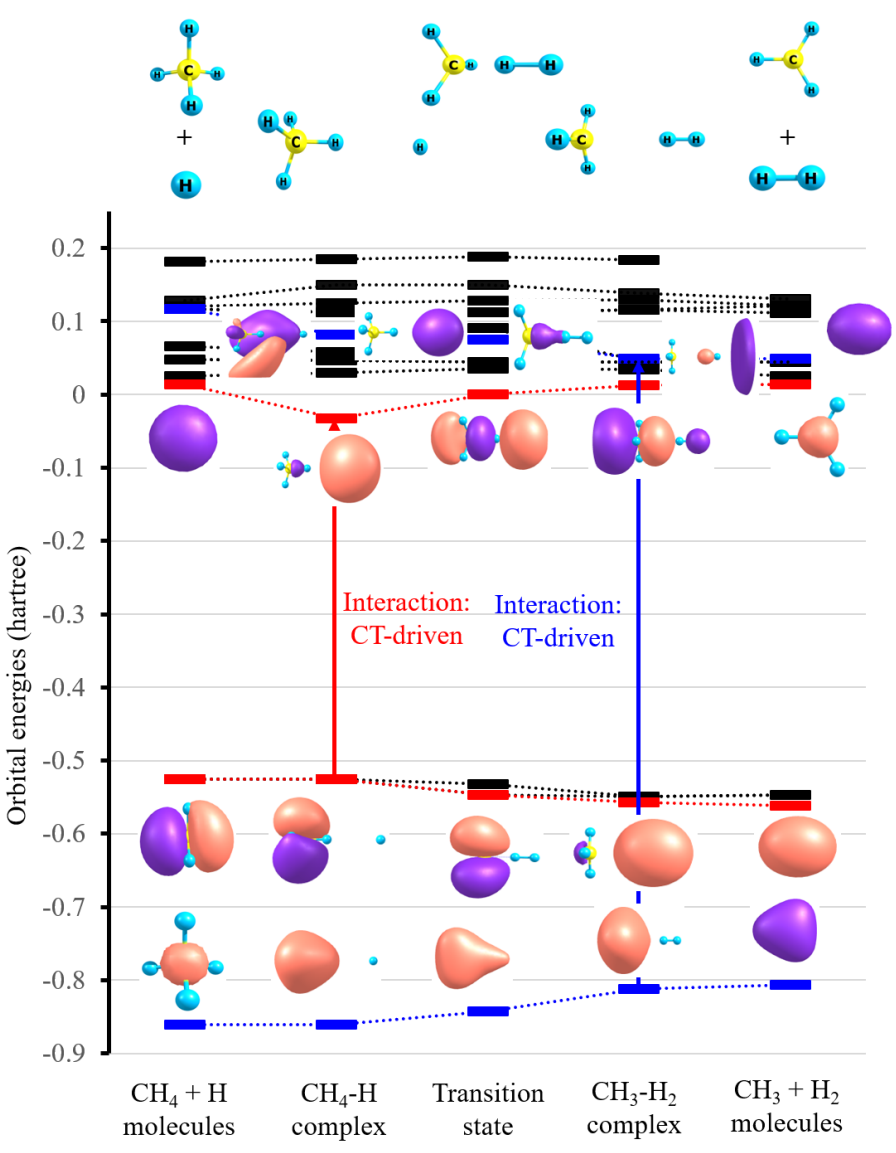
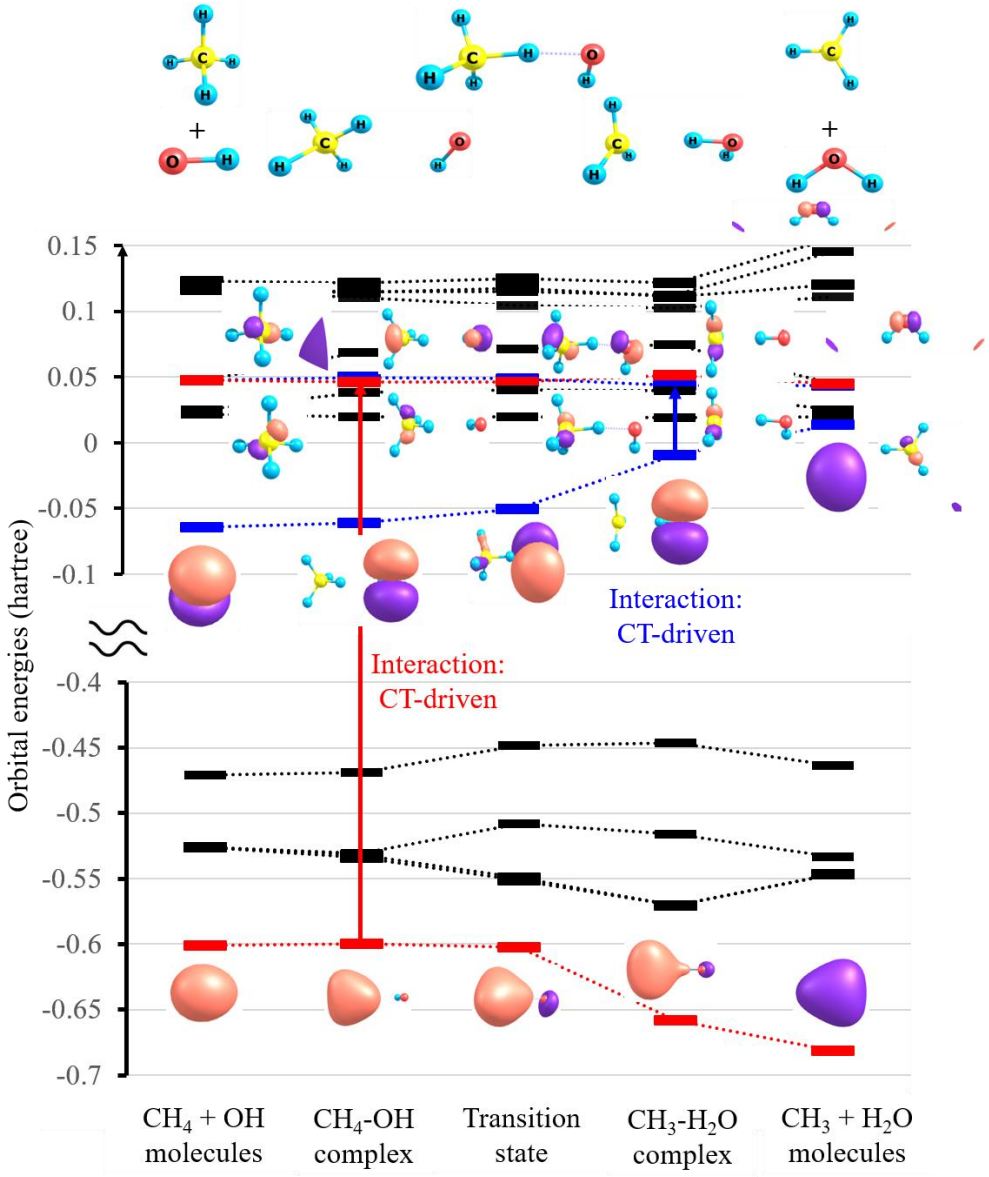
Fig. S1. Reactive orbital energy diagrams of fundamental reactions. Reaction numbers correspond to those in Table 1. LC-BLYP+LRD/aug-cc-pVTZ calculations.



Reaction 3



Reaction 4



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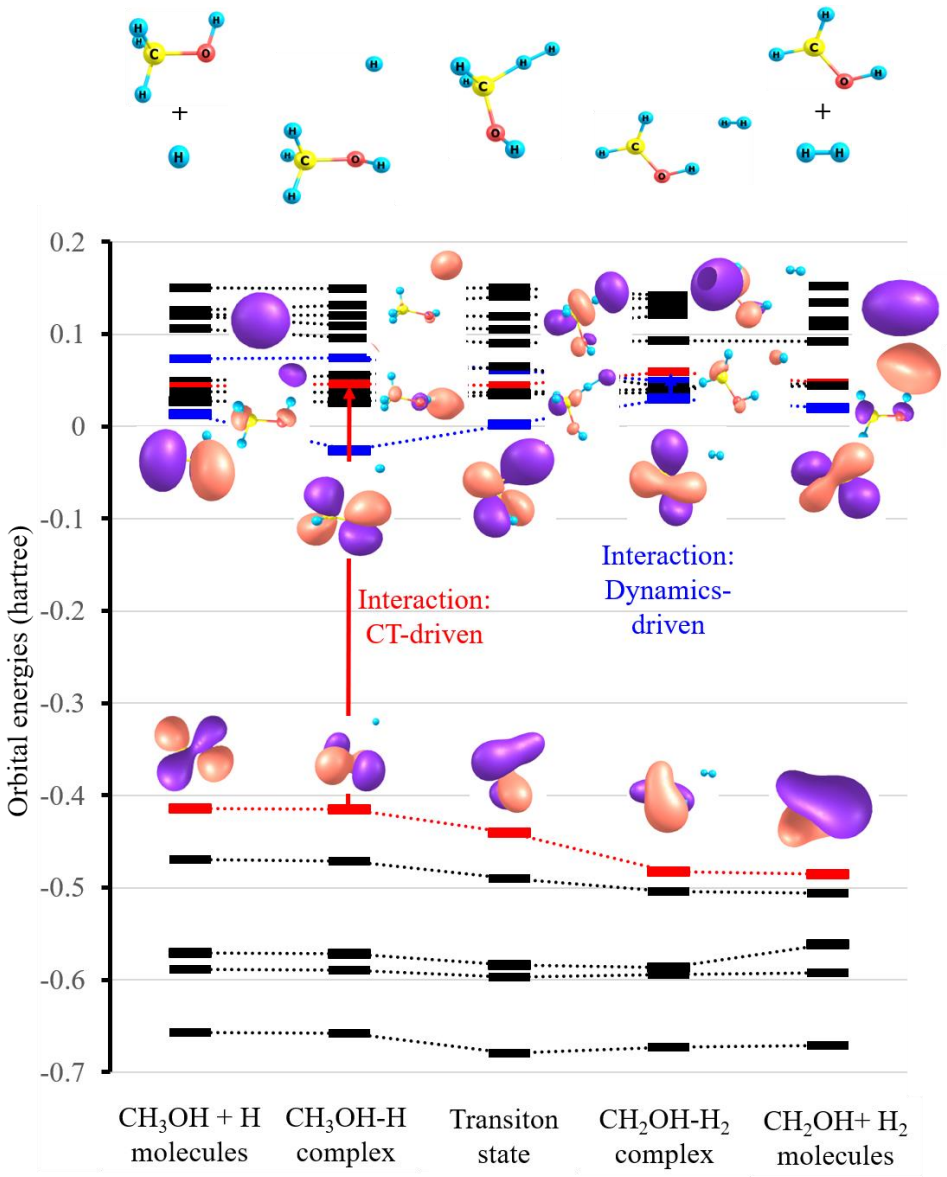
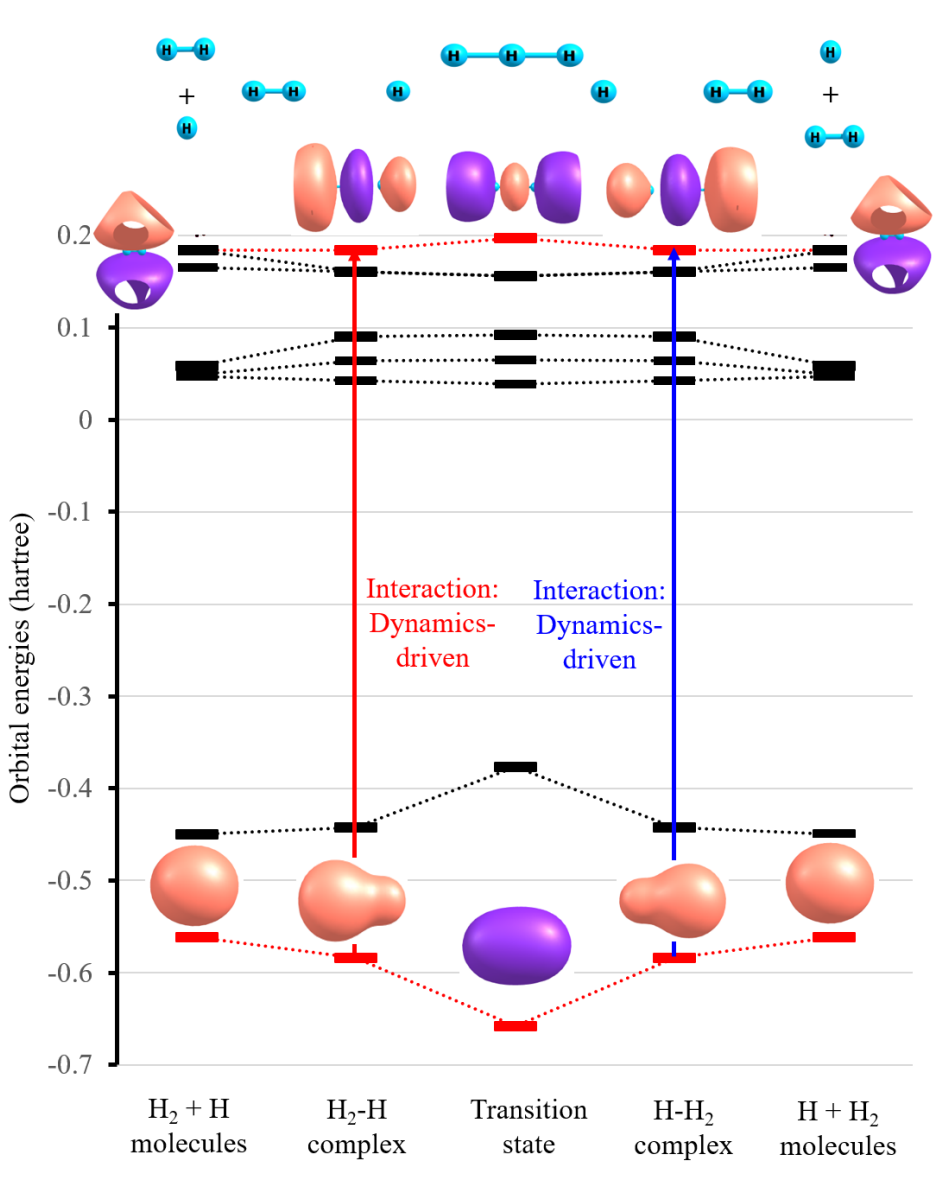
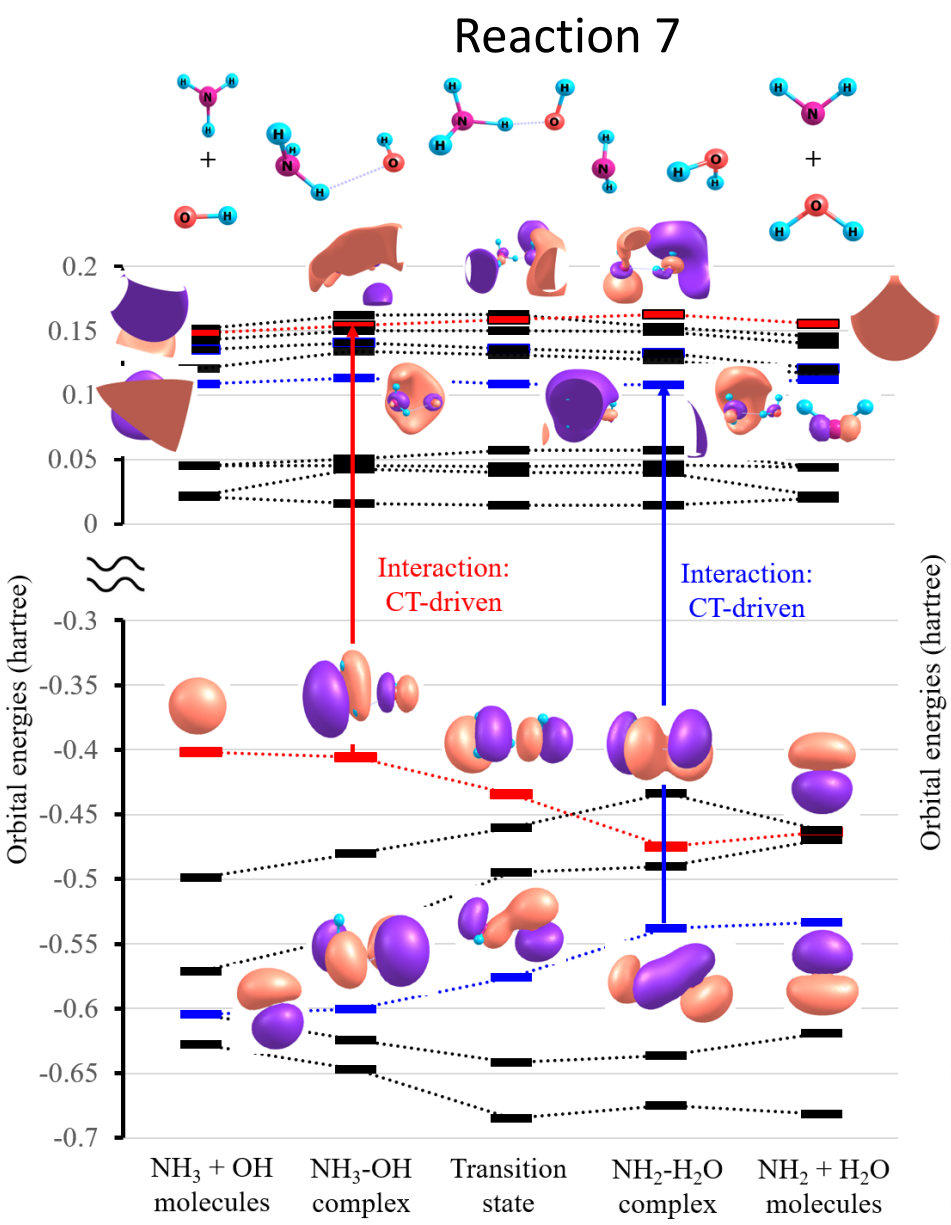
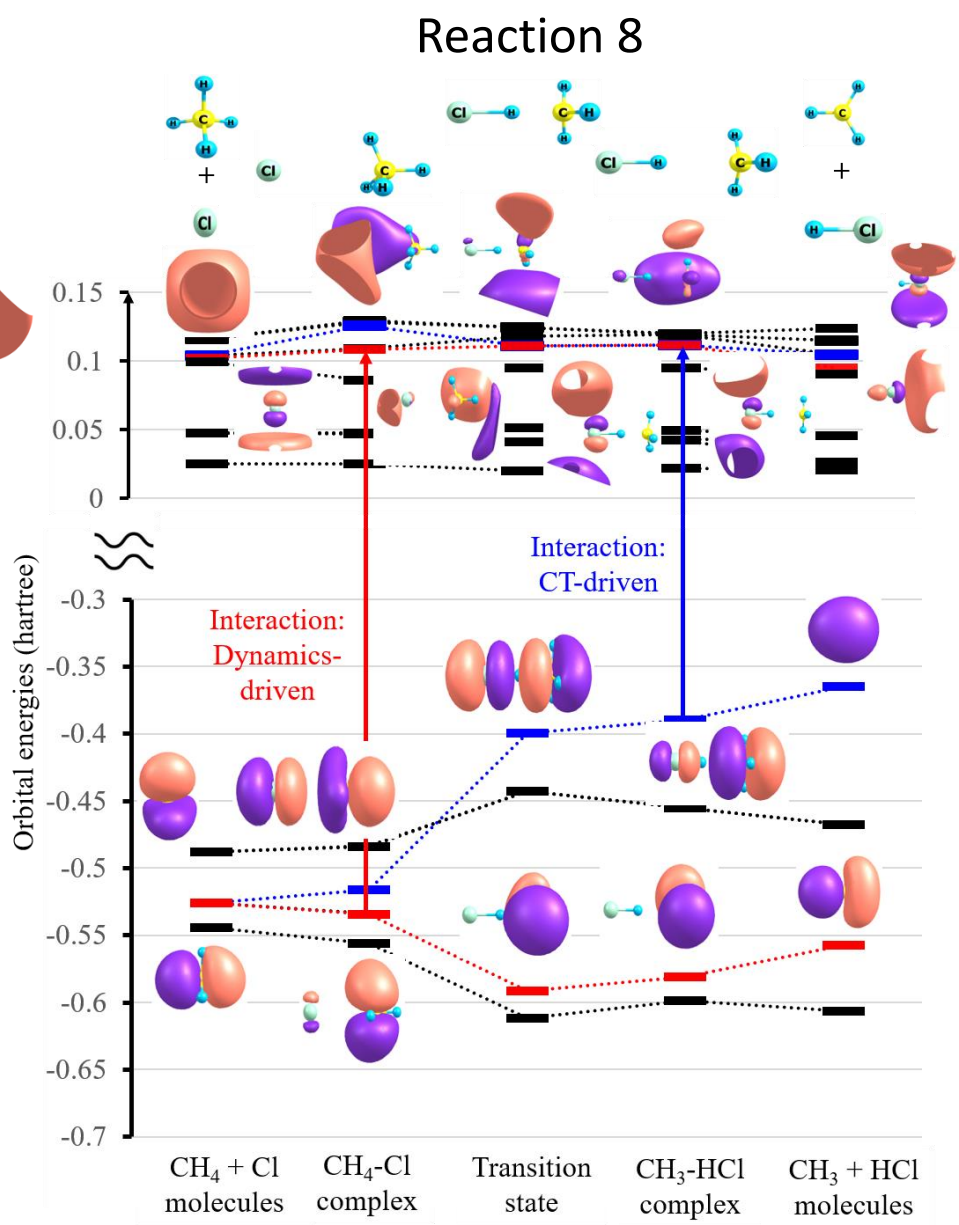


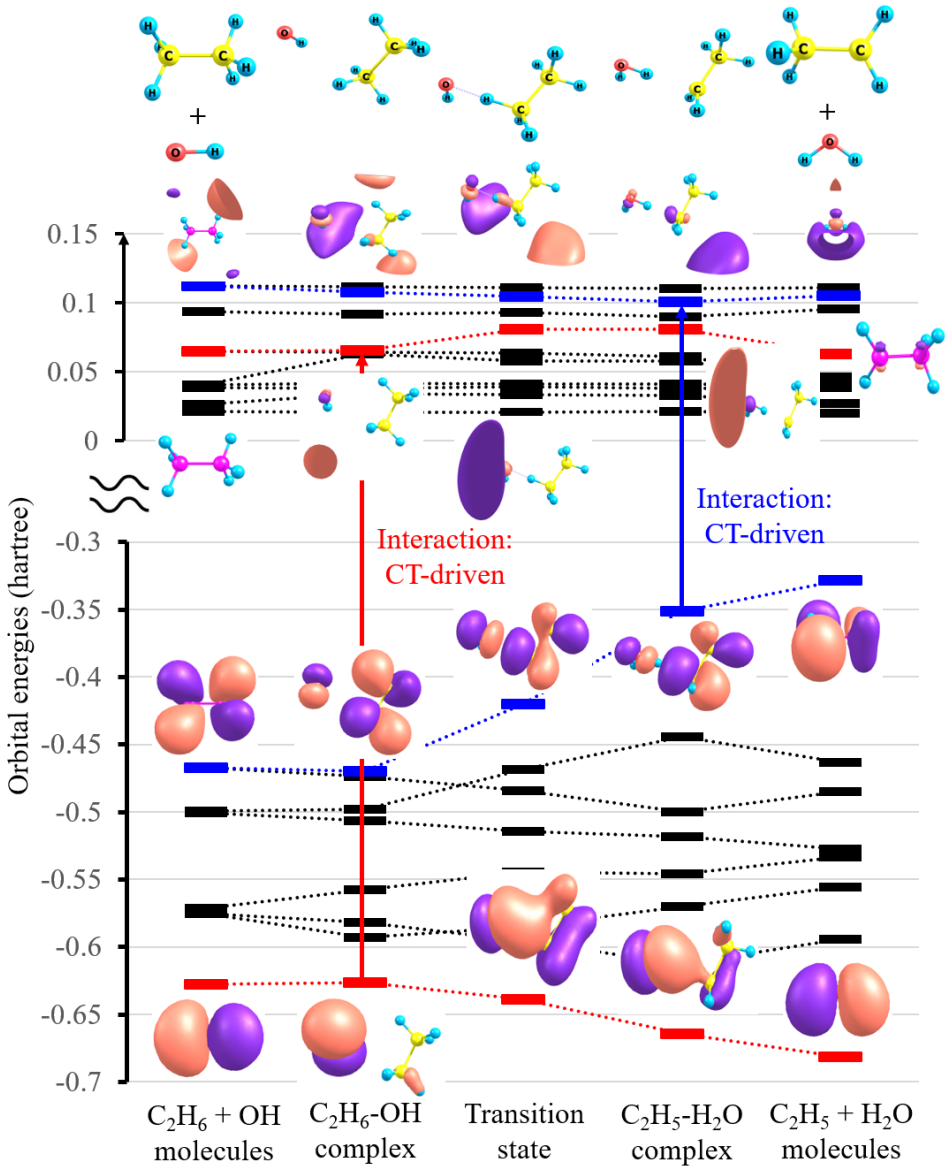
Reaction 6




Reaction 7
Orbital energies (hartree)
0.2
0.15
0.1
0.05
0
-0.3
-0.35
-0.4
-0.45
-0.5
-0.55
-0.6
-0.65
-0.7
Interaction:
CT-driven
Interaction:
CT-driven
NH3 + OH molecules
NH3-OH complex
Transition state
NH2-H2O complex
NH2 + H2O molecules

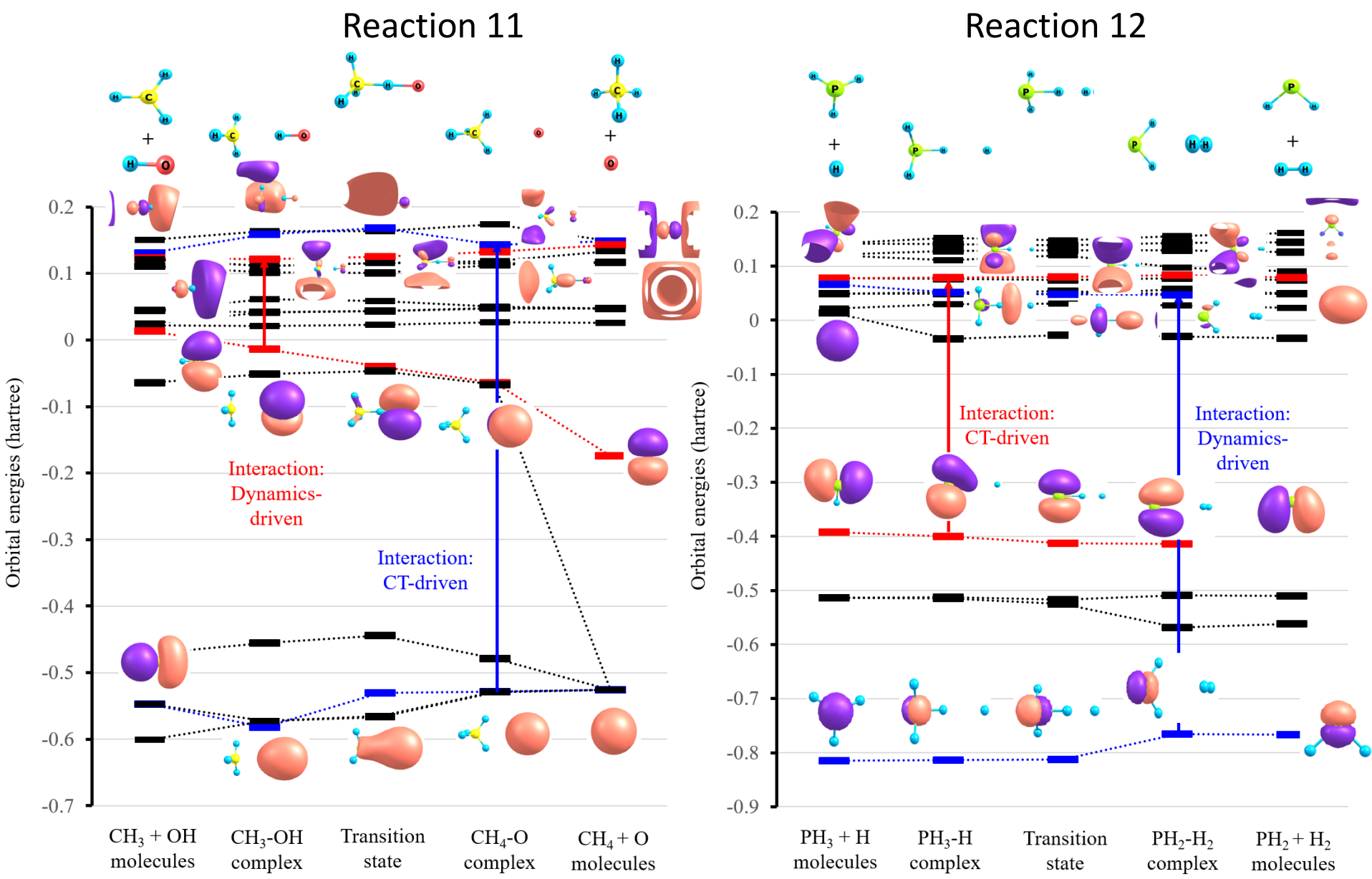

Reaction 8
Orbital energies (hartree)
0.15
0.1
0.05
0
-0.3
-0.35
-0.4
-0.45
-0.5
-0.55
-0.6
-0.65
-0.7
Interaction:
Dynamics-driven
Interaction:
CT-driven
CH4 + Cl molecules
CH4-Cl complex
Transition state
CH3-HCl complex
CH3 + HCl molecules

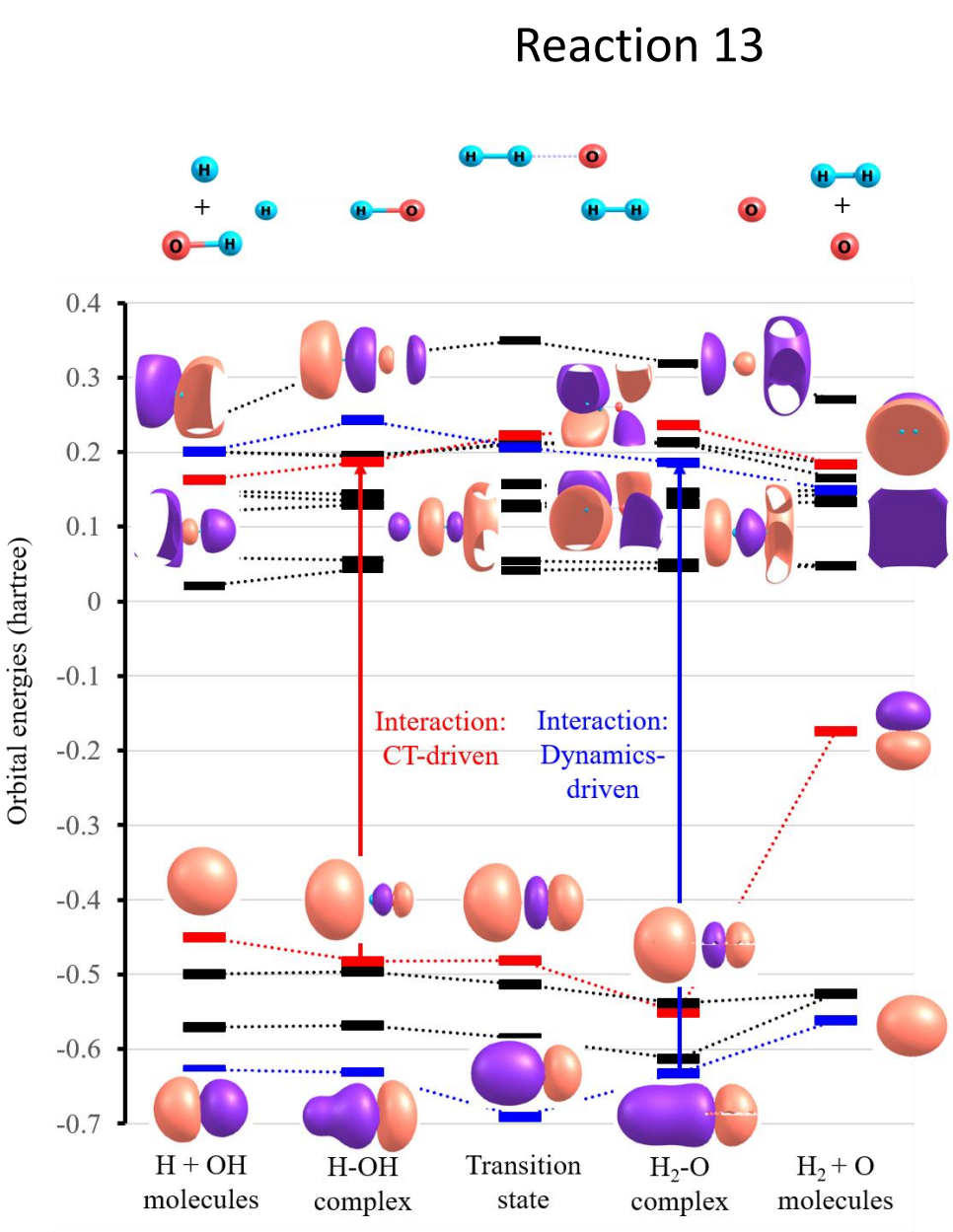
Reaction 9

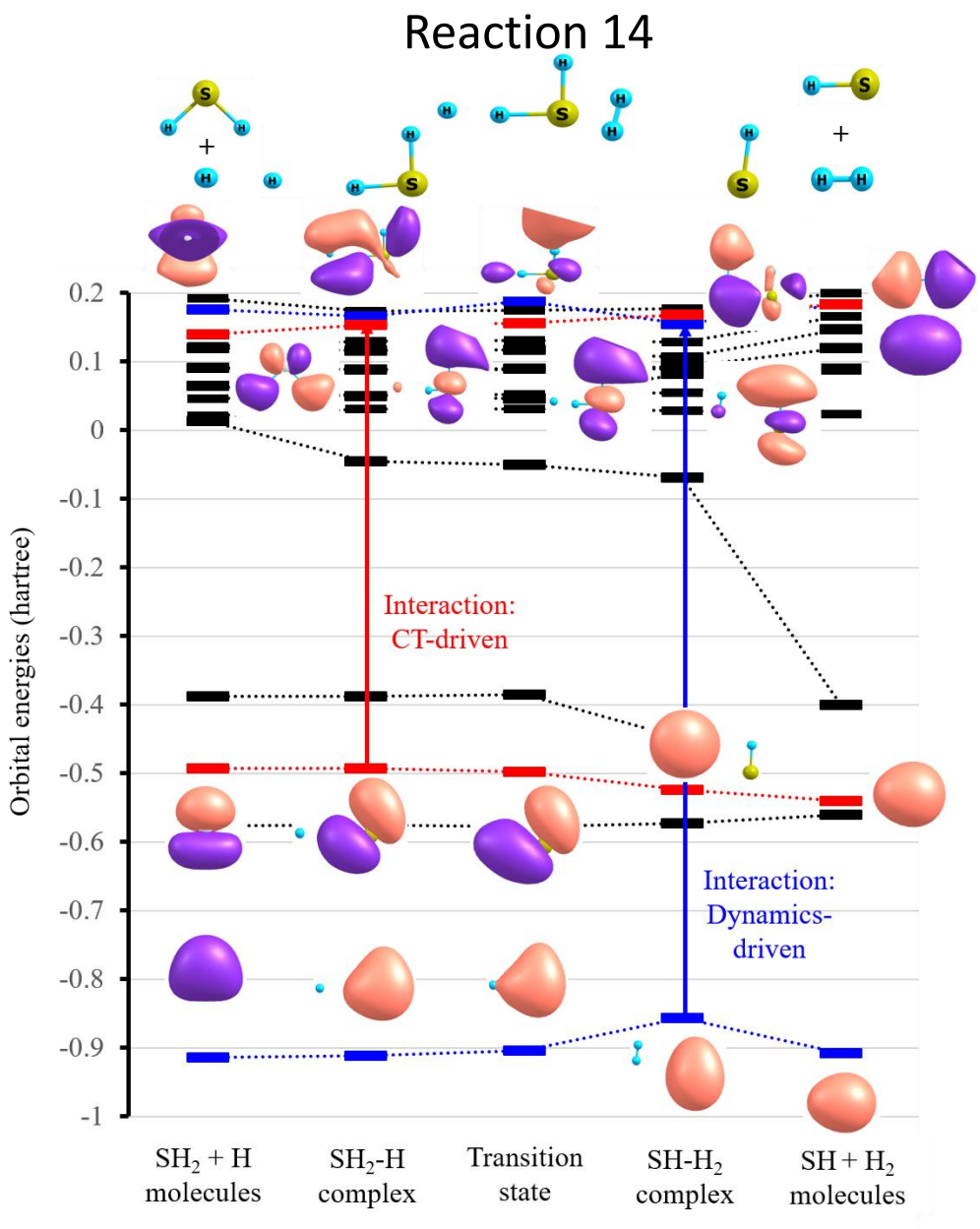


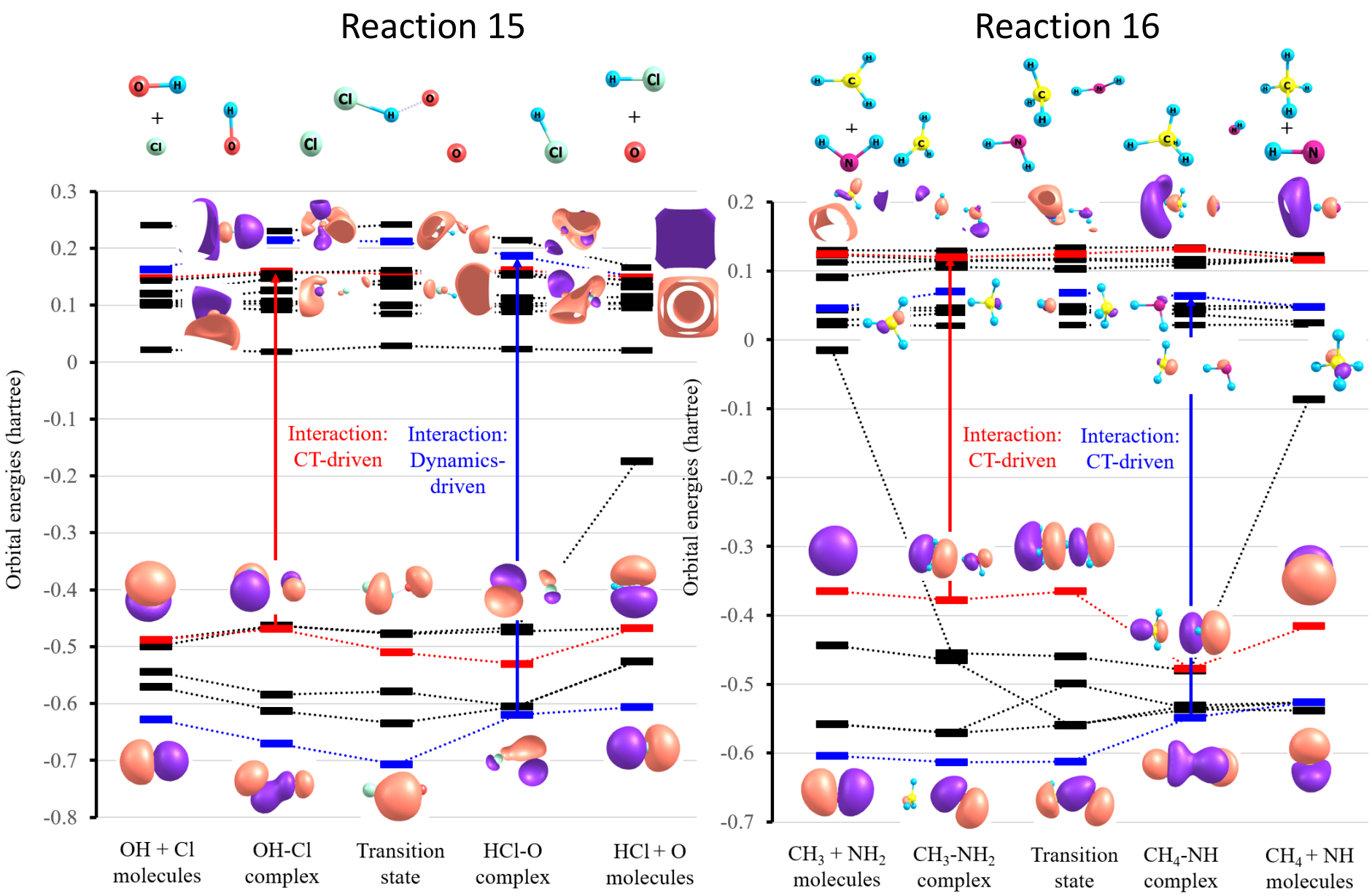
Reaction 10

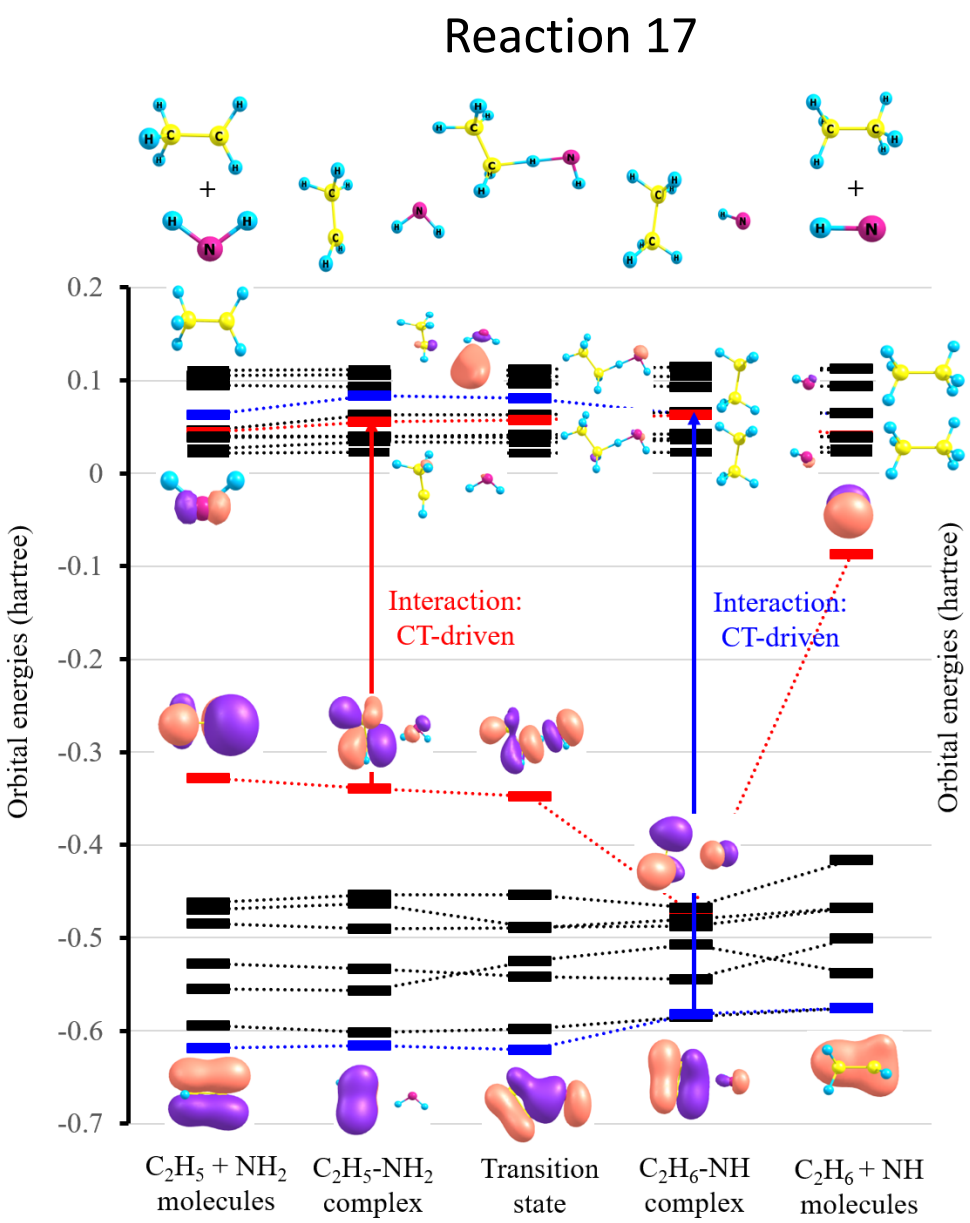
No TS

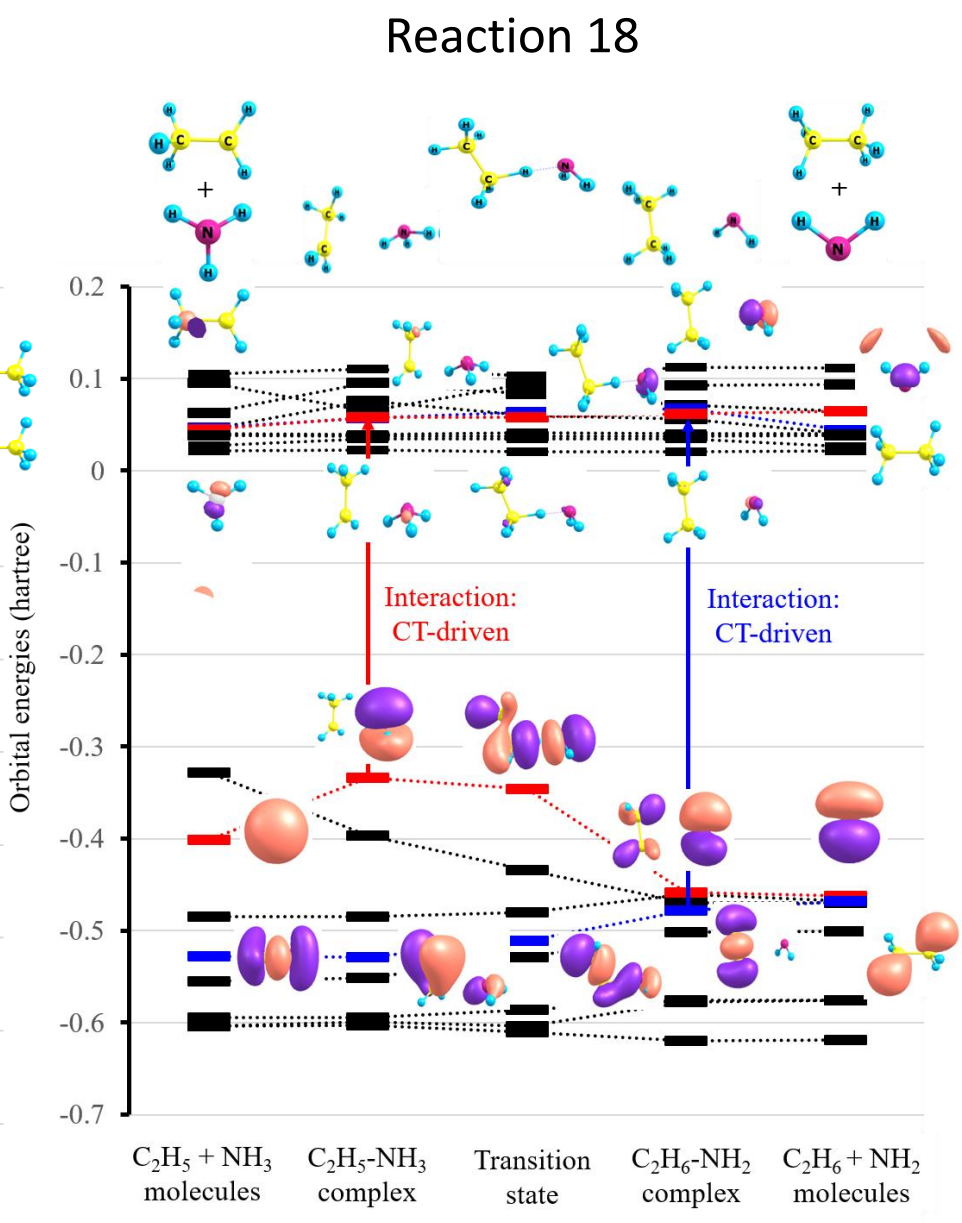

Reaction 11
Reaction 12
Orbital energies (hartree)
Interaction: Dynamics-driven
Interaction: CT-driven
Interaction: CT-driven
Interaction: Dynamics-driven
CH3 + OH molecules
CH3-OH complex
Transition state
CH4-O complex
CH4 + O molecules
PH3 + H molecules
PH3-H complex
Transition state
PH2-H2 complex
PH2 + H2 molecules


Reaction 13
Orbital energies (hartree)
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
Interaction: CT-driven
Interaction: Dynamics-driven
H + OH molecules
H-OH complex
Transition state
H2-O complex
H2 + O molecules

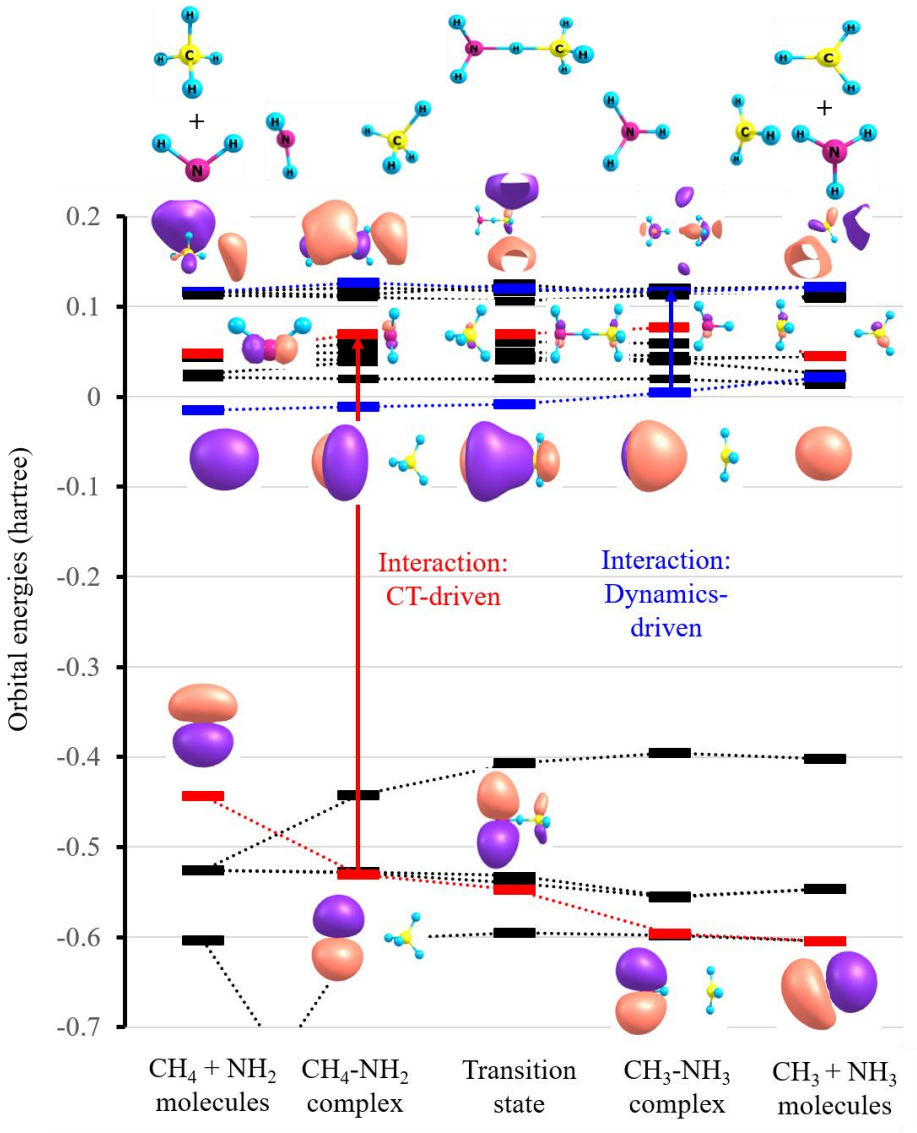

Reaction 14
Orbital energies (hartree)
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
Interaction: CT-driven
Interaction: Dynamics-driven
SH2 + H molecules
SH2-H complex
Transition state
SH-H2 complex
SH + H2 molecules


Reaction 15
Reaction 16
Orbital energies (hartree)
Interaction: CT-driven
Interaction: Dynamics-driven
Interaction: CT-driven
Interaction: CT-driven
OH + Cl molecules
OH-Cl complex
Transition state
HCl-O complex
HCl + O molecules
CH3 + NH2 molecules
CH3-NH2 complex
Transition state
CH4-NH complex
CH4 + NH molecules

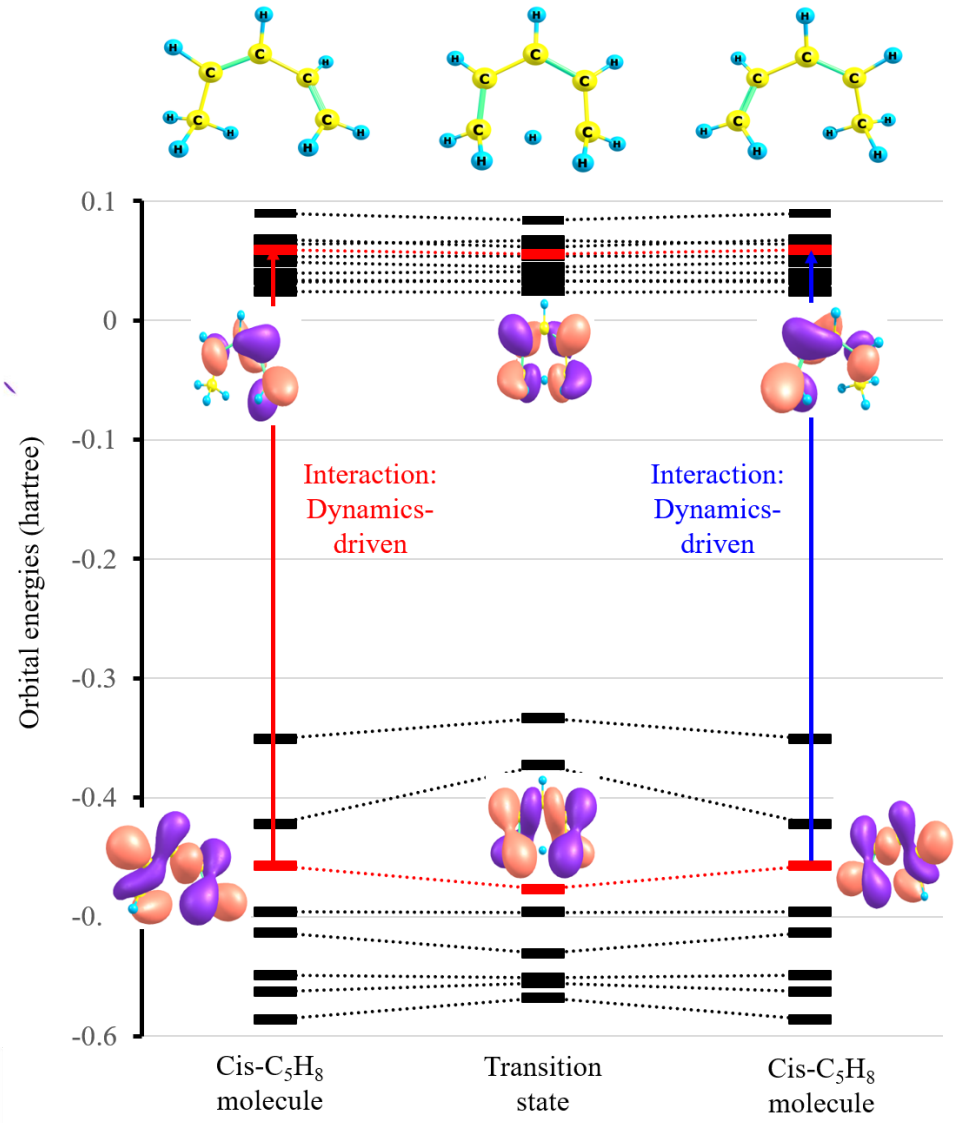

Reaction 17
Orbital energies (hartree)
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
Interaction:
CT-driven
Interaction:
CT-driven
$C_2H_5 + NH_2$ molecules
C_2H_5-NH_2 complex
Transition state
C_2H_6-NH complex
$C_2H_6 + NH$ molecules


Reaction 18
Orbital energies (hartree)
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
Interaction:
CT-driven
Interaction:
CT-driven
$C_2H_5 + NH_3$ molecules
C_2H_5-NH_3 complex
Transition state
C_2H_6-NH_2 complex
$C_2H_6 + NH_2$ molecules

Reaction 19



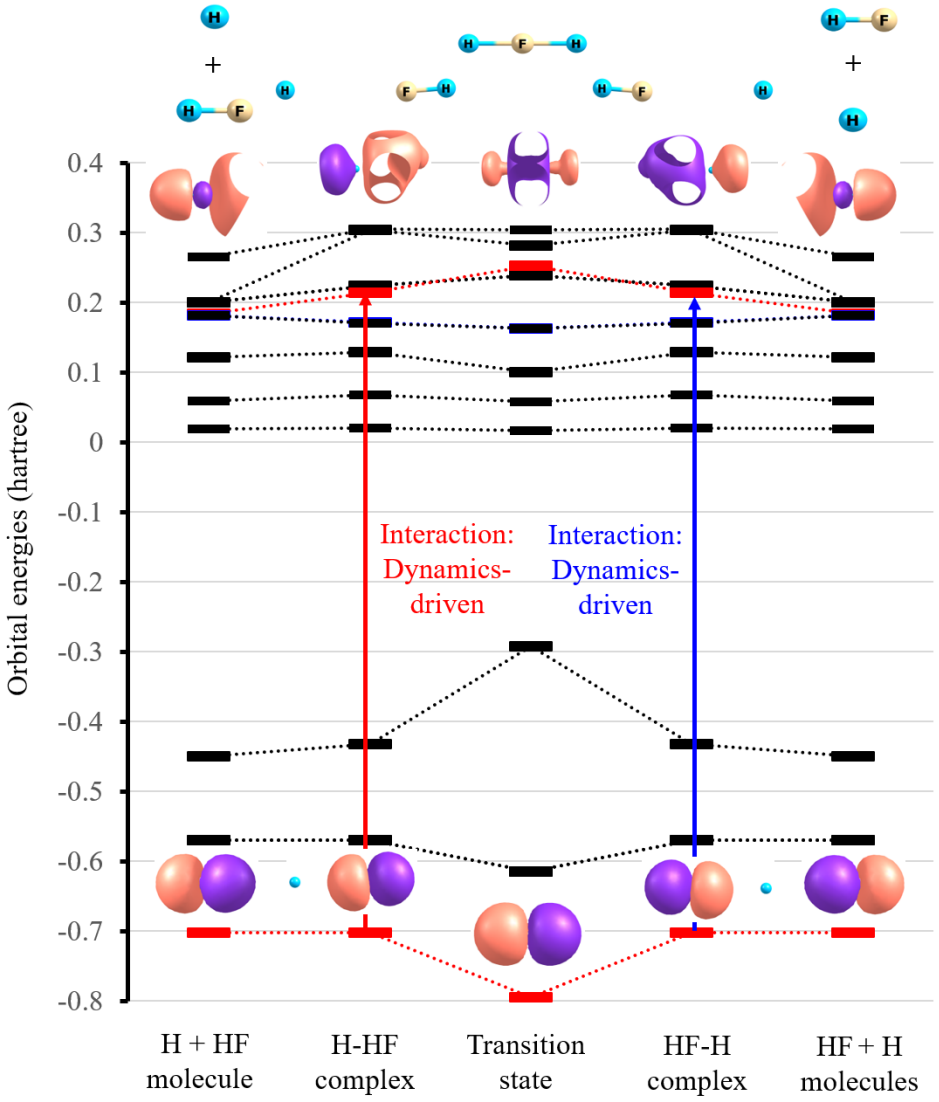
Reaction 20

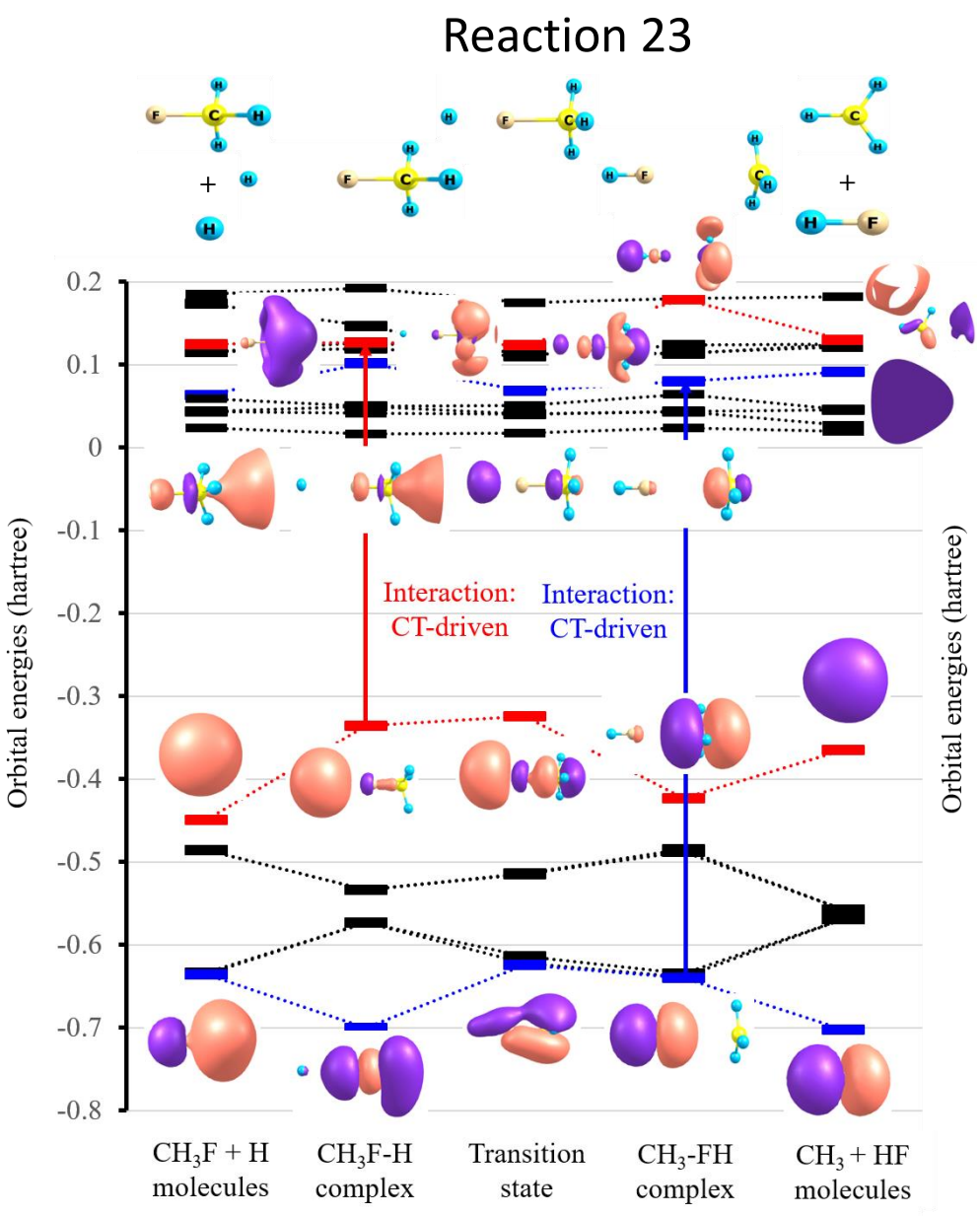


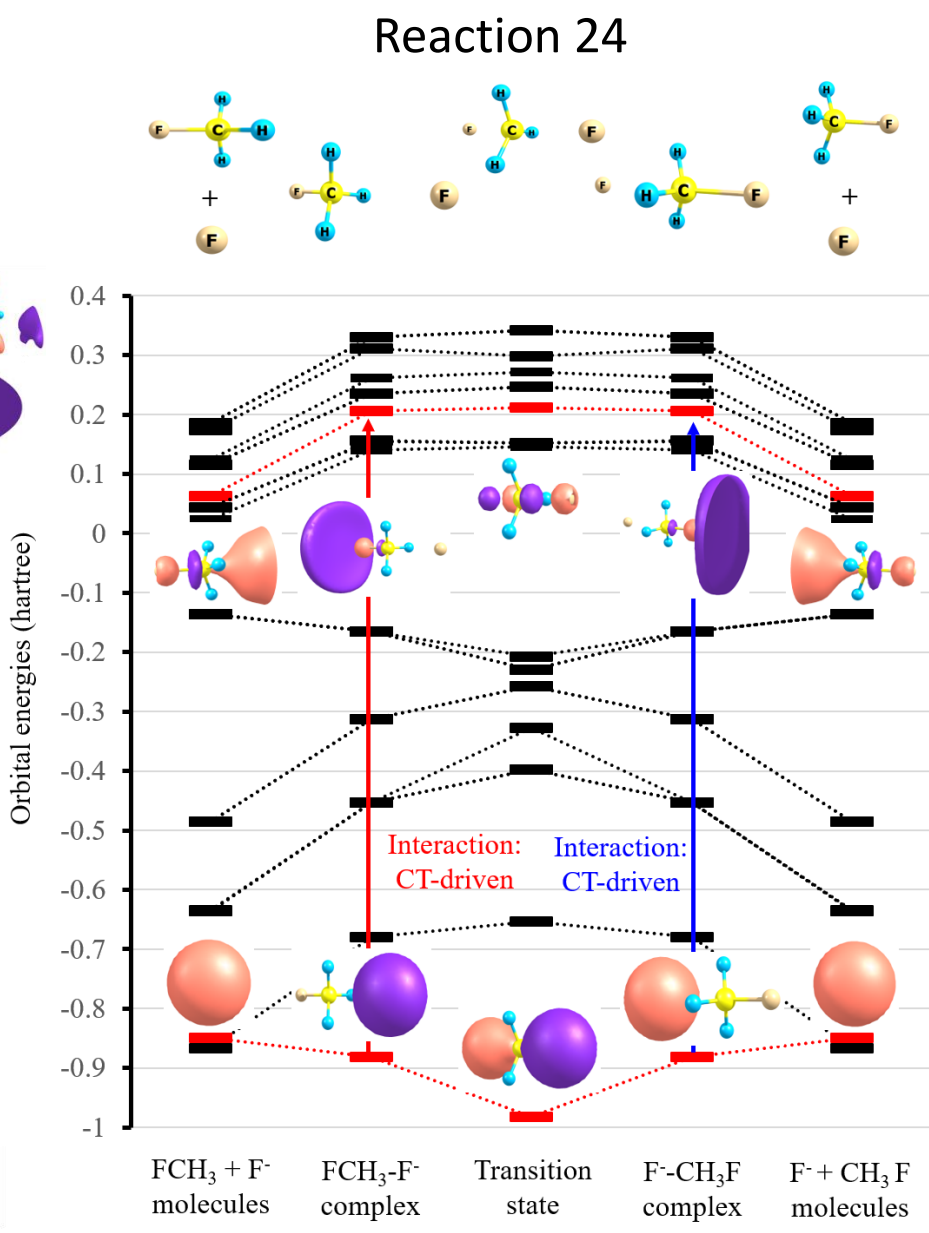
Reaction 21

No TS

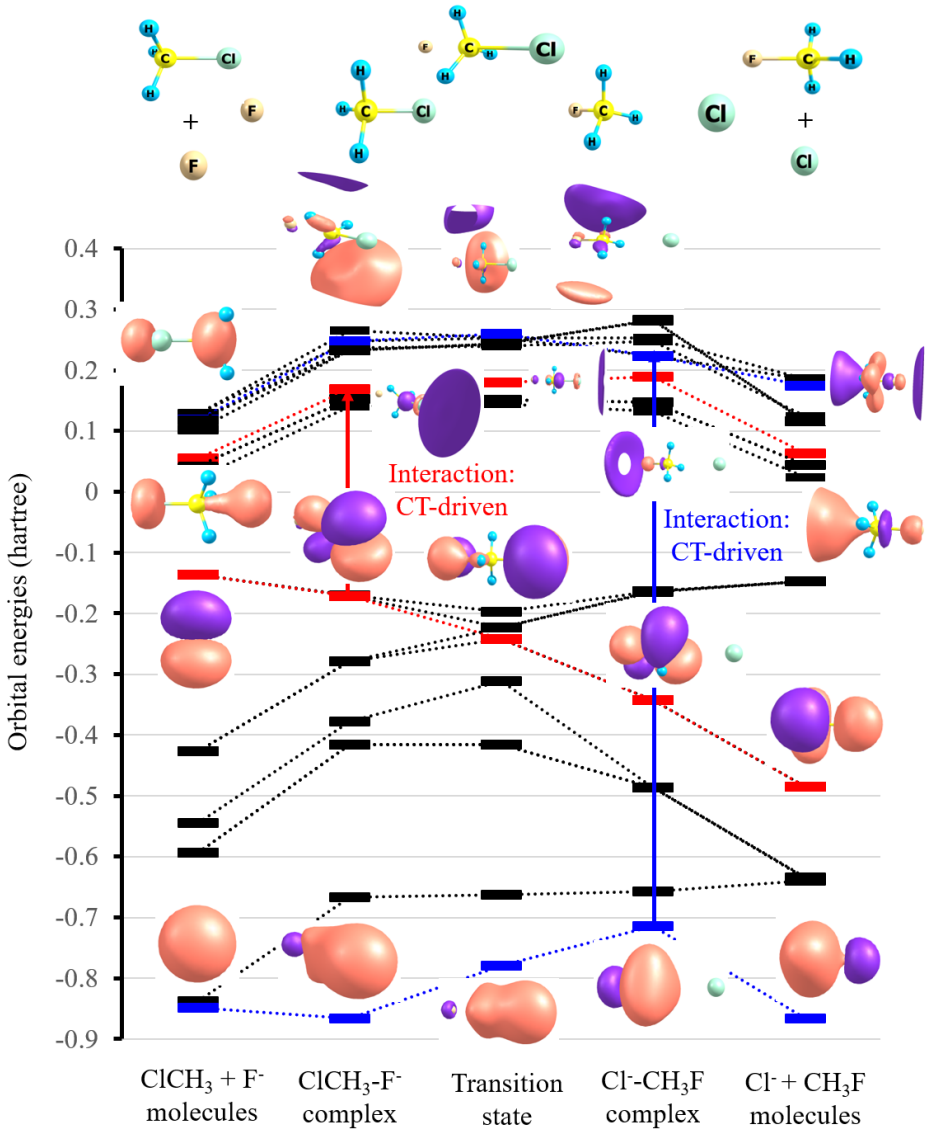
Reaction 22



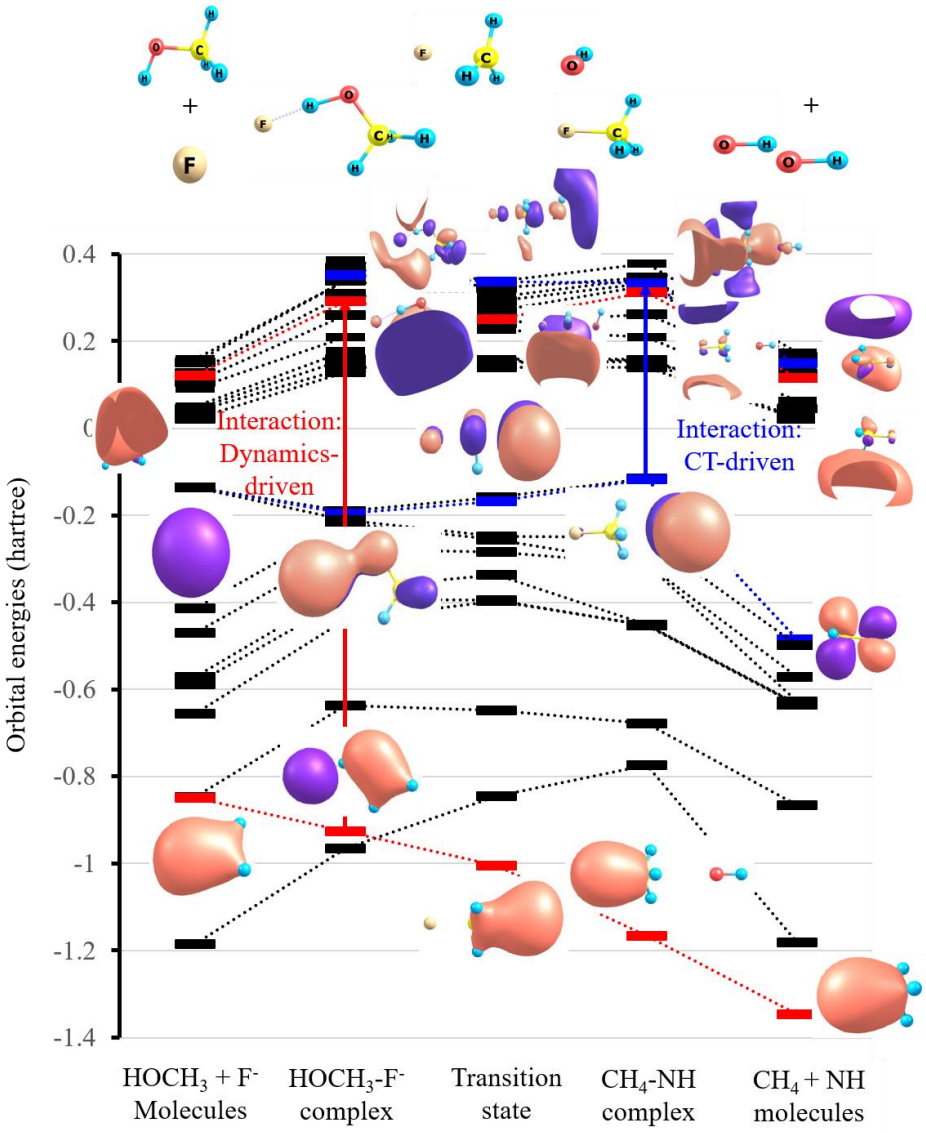

Reaction 23
Orbital energies (hartree)
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
Interaction: CT-driven
Interaction: CT-driven
CH3F + H molecules
CH3F-H complex
Transition state
CH3-FH complex
CH3 + HF molecules

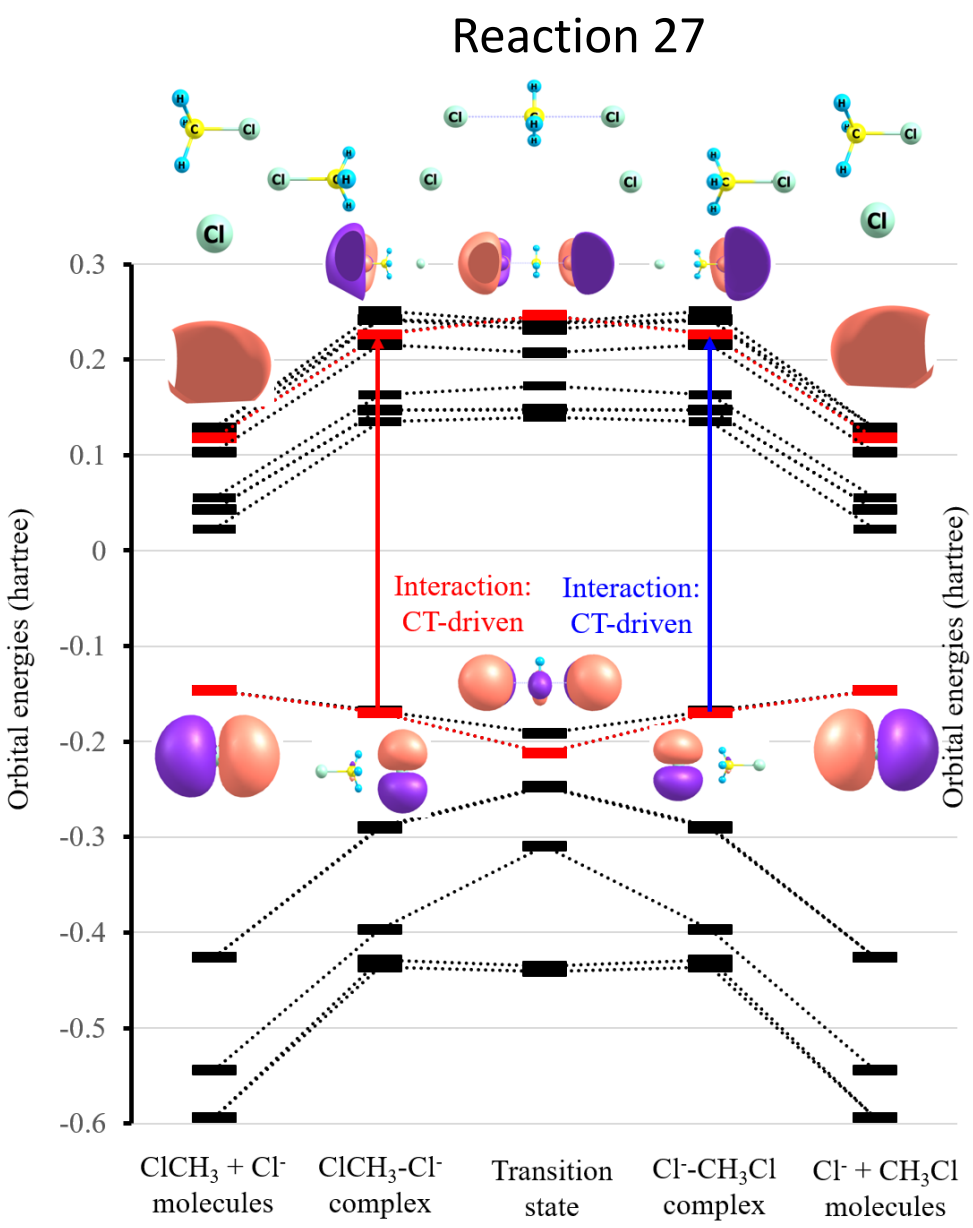

Reaction 24
Orbital energies (hartree)
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
Interaction: CT-driven
Interaction: CT-driven
FCH3 + F- molecules
FCH3-F- complex
Transition state
F--CH3F complex
F- + CH3 F molecules

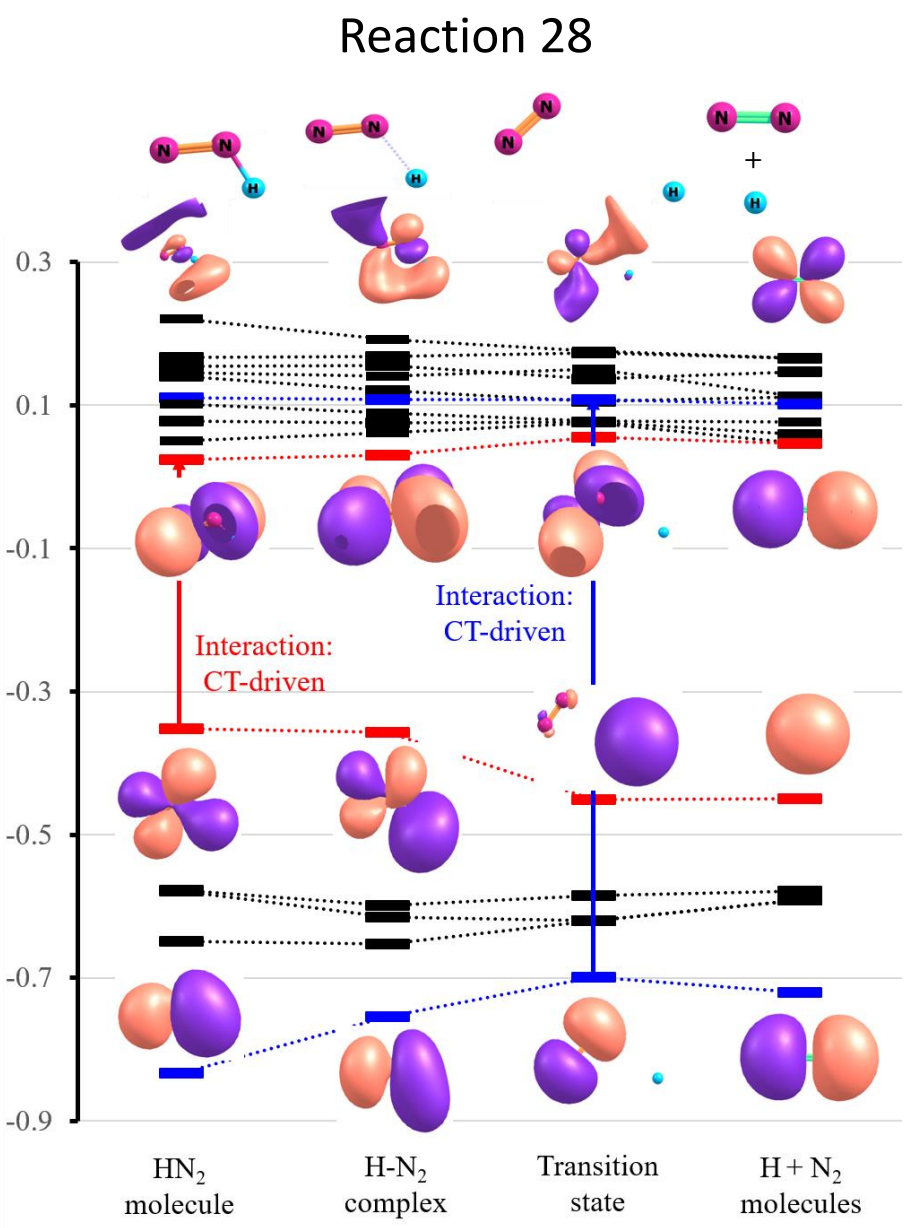
Reaction 25

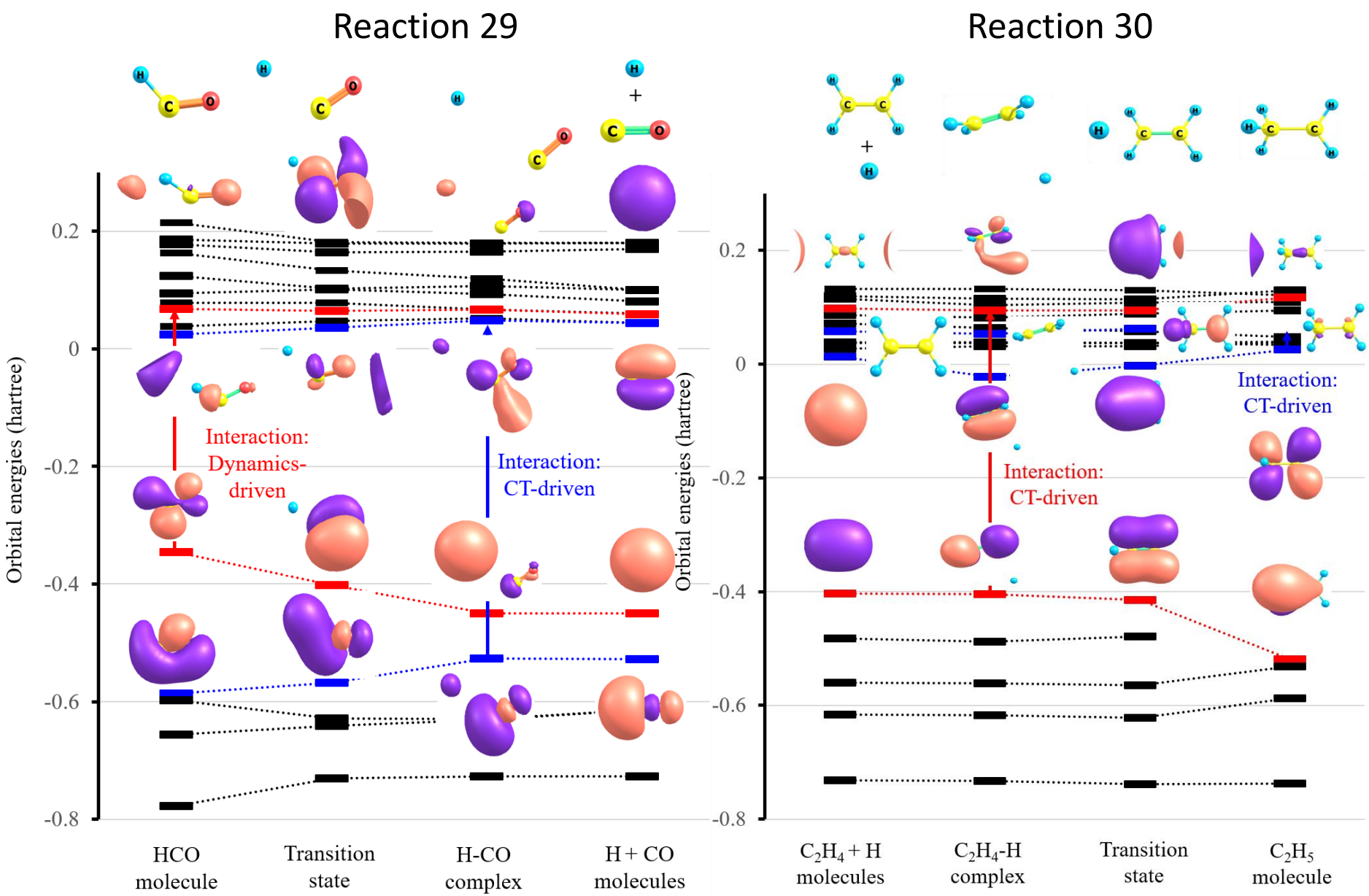


Reaction 26

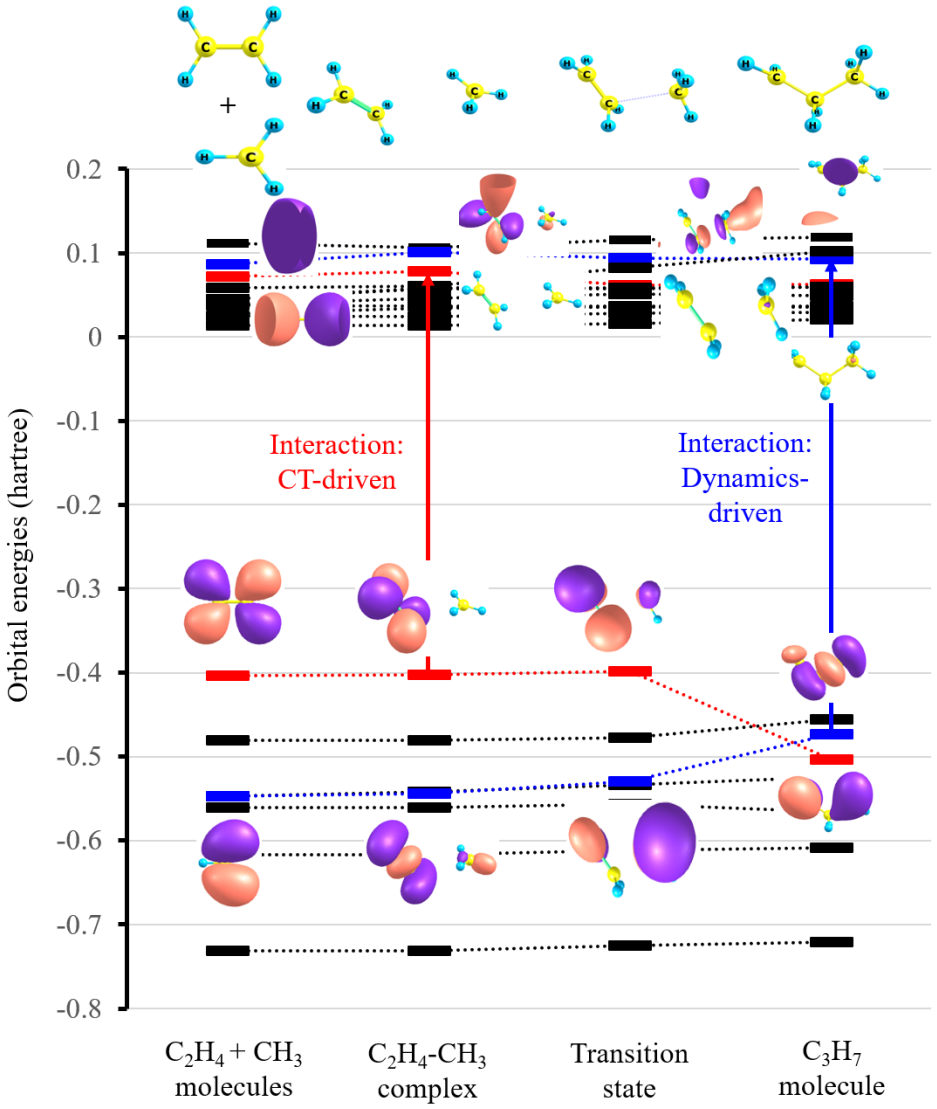



Reaction 27
Orbital energies (hartree)
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
Interaction: CT-driven
Interaction: CT-driven
ClCH3 + Cl- molecules
ClCH3-Cl- complex
Transition state
Cl--CH3Cl complex
Cl- + CH3Cl molecules

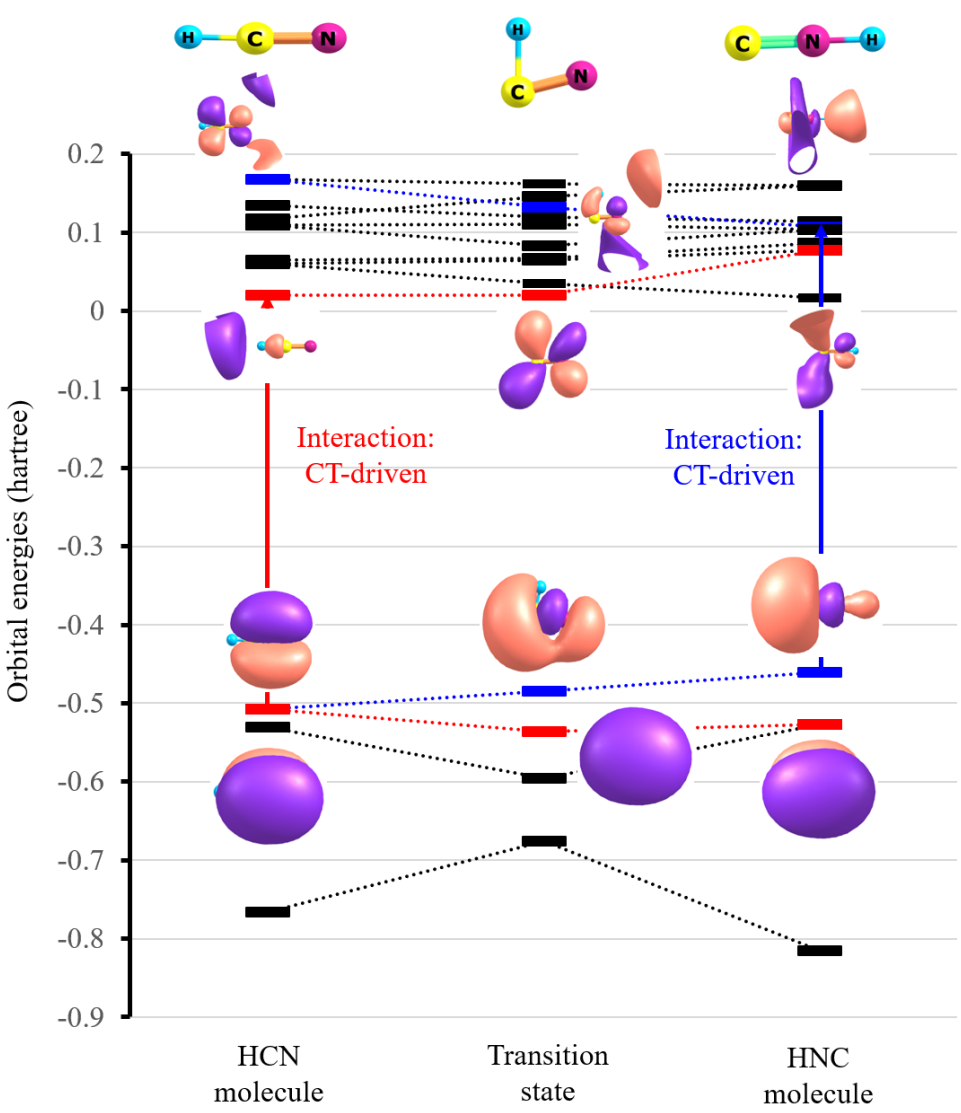

Reaction 28
Orbital energies (hartree)
0.3
0.1
-0.1
-0.3
-0.5
-0.7
-0.9
Interaction: CT-driven
Interaction: CT-driven
HN2 molecule
H-N2 complex
Transition state
H + N2 molecules

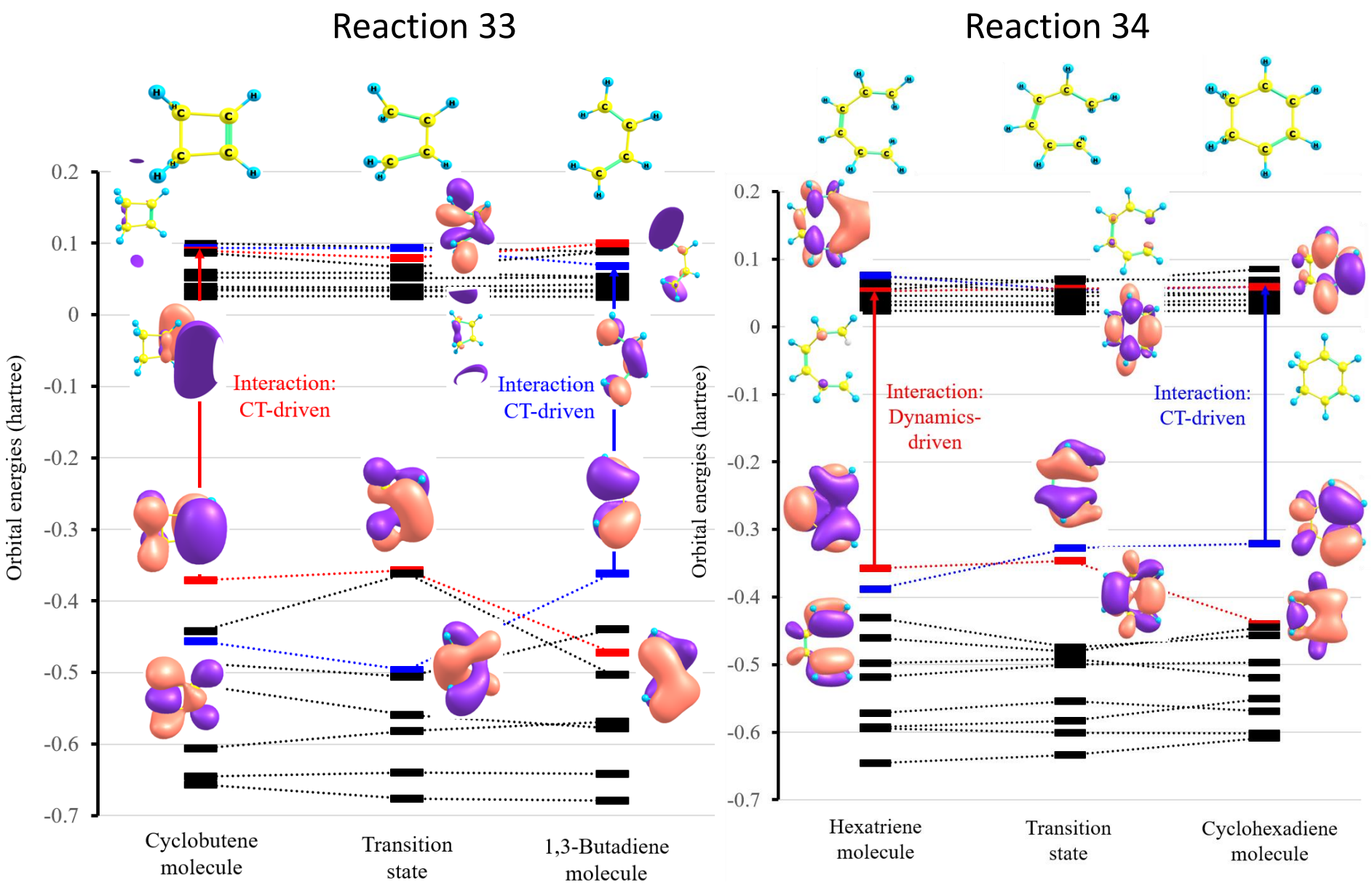

Reaction 29
Reaction 30
Orbital energies (hartree)
0.2
0
-0.2
-0.4
-0.6
-0.8
Interaction: Dynamics-driven
Interaction: CT-driven
Interaction: CT-driven
Interaction: CT-driven
HCO molecule
Transition state
H-CO complex
H + CO molecules
C_2H_4 + H molecules
C_2H_4-H complex
Transition state
C_2H_5 molecule

Reaction 31

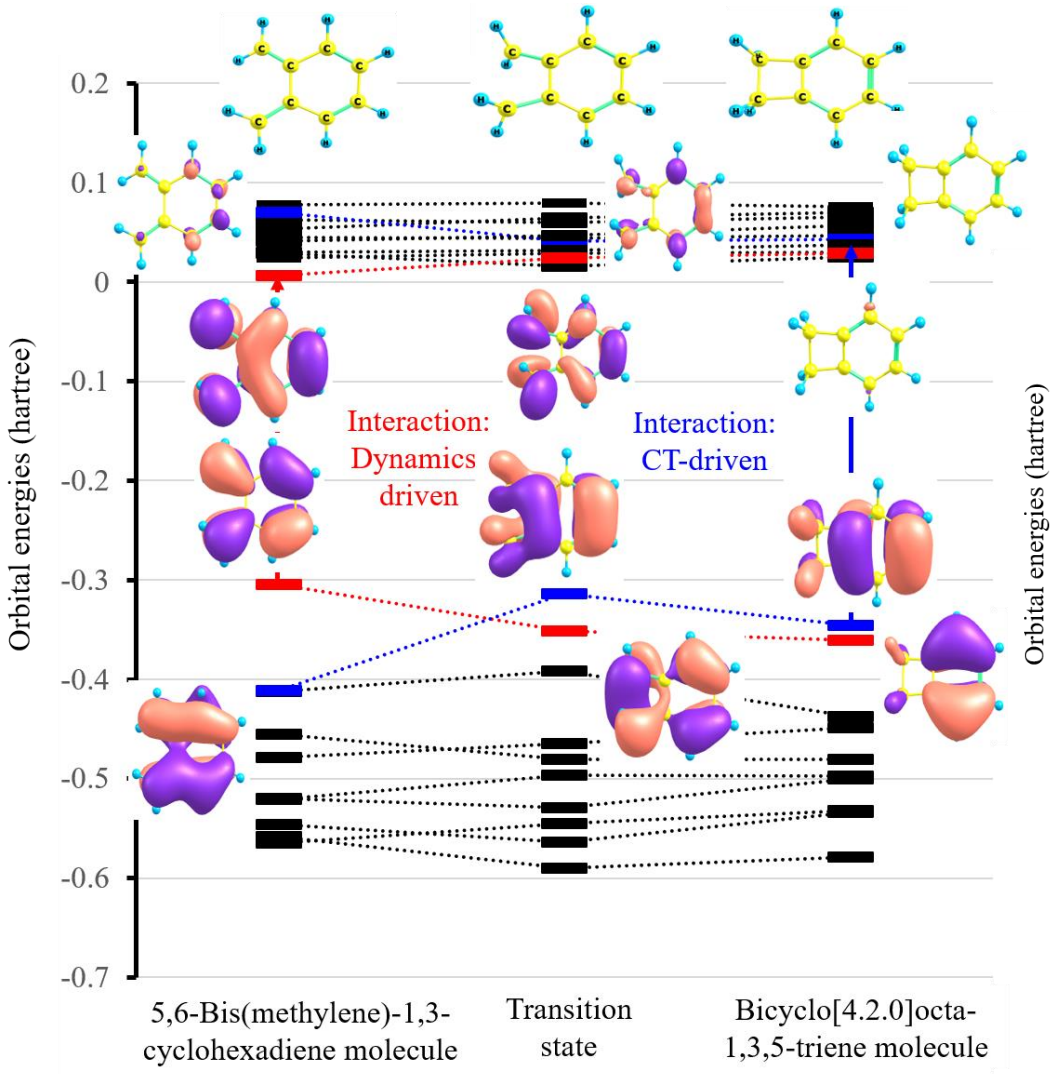


Reaction 32

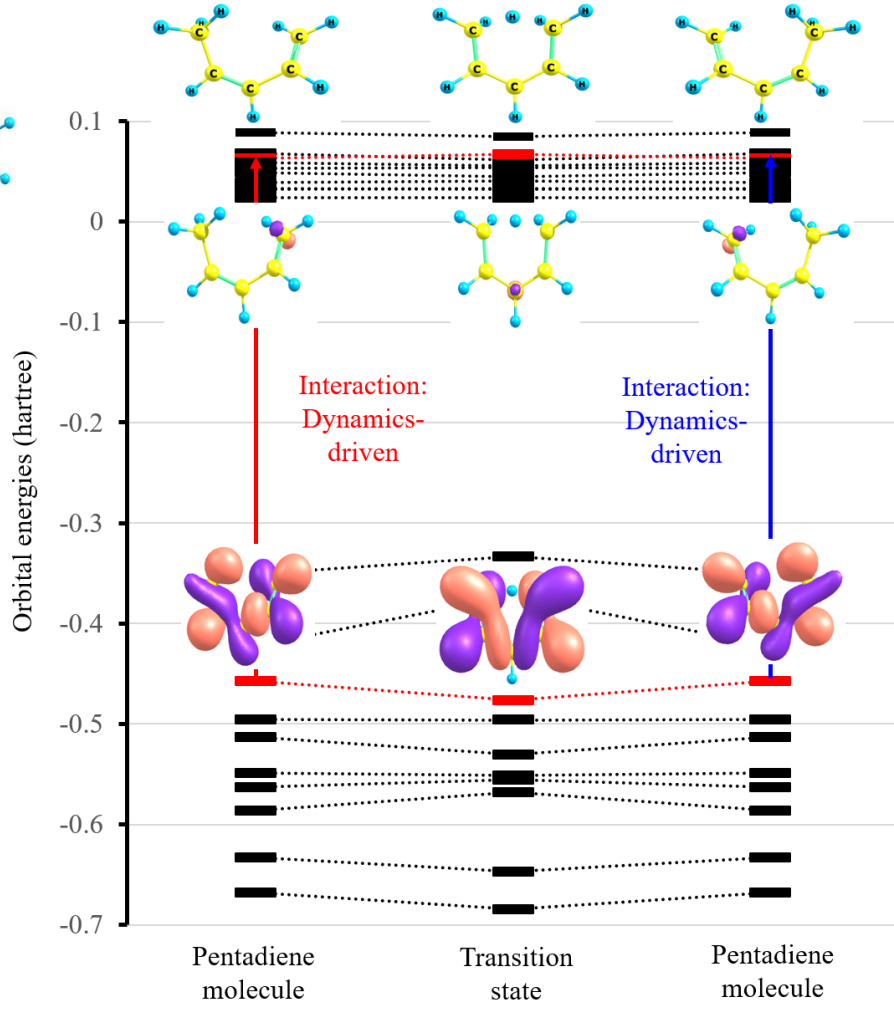


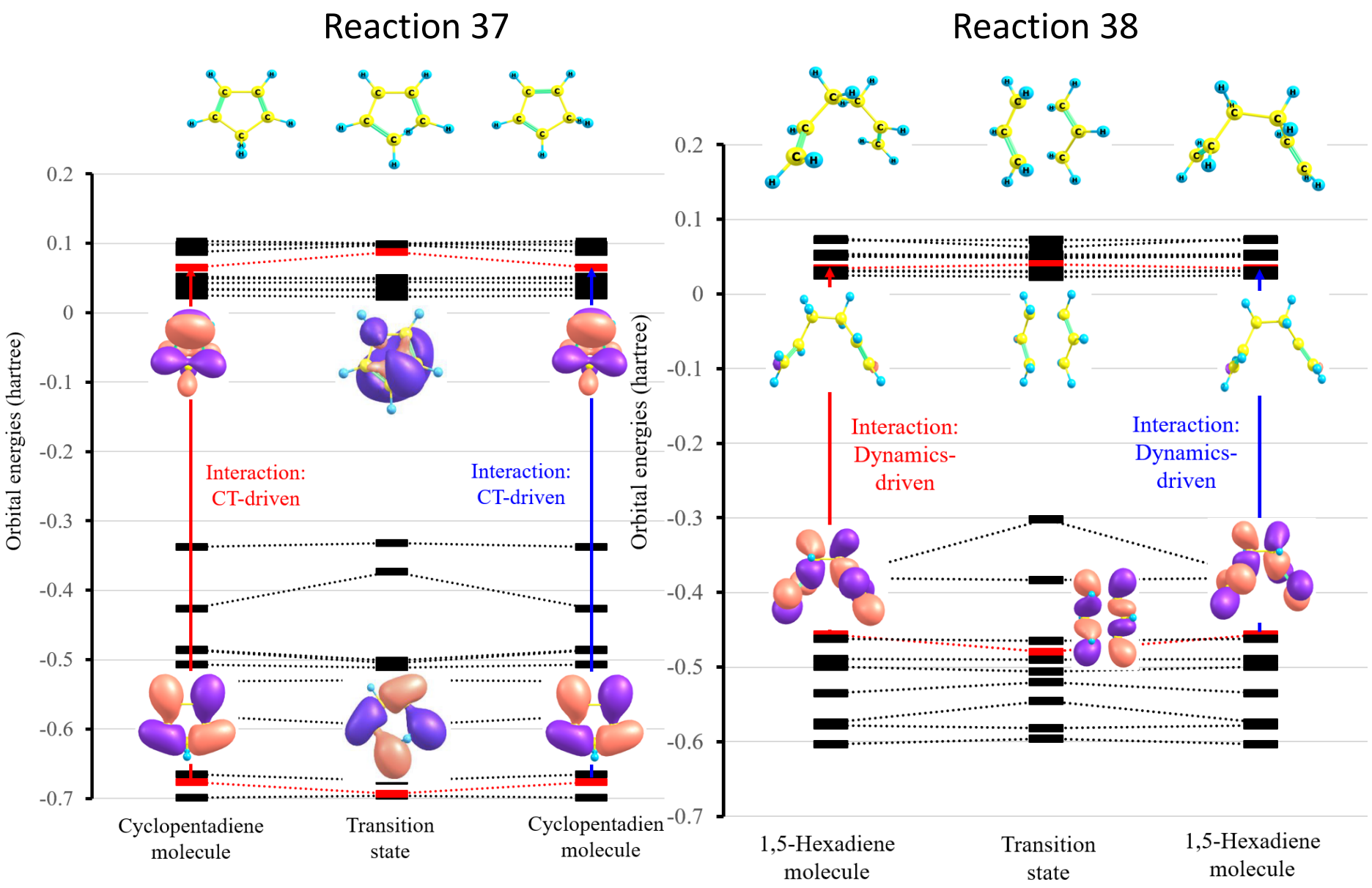

Reaction 33
Orbital energies (hartree)
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
Interaction:
CT-driven
Interaction
CT-driven
Cyclobutene
molecule
Transition
state
1,3-Butadiene
molecule
Reaction 34
Orbital energies (hartree)
Interaction:
Dynamics-
driven
Interaction:
CT-driven
Hexatriene
molecule
Transition
state
Cyclohexadiene
molecule

Reaction 35

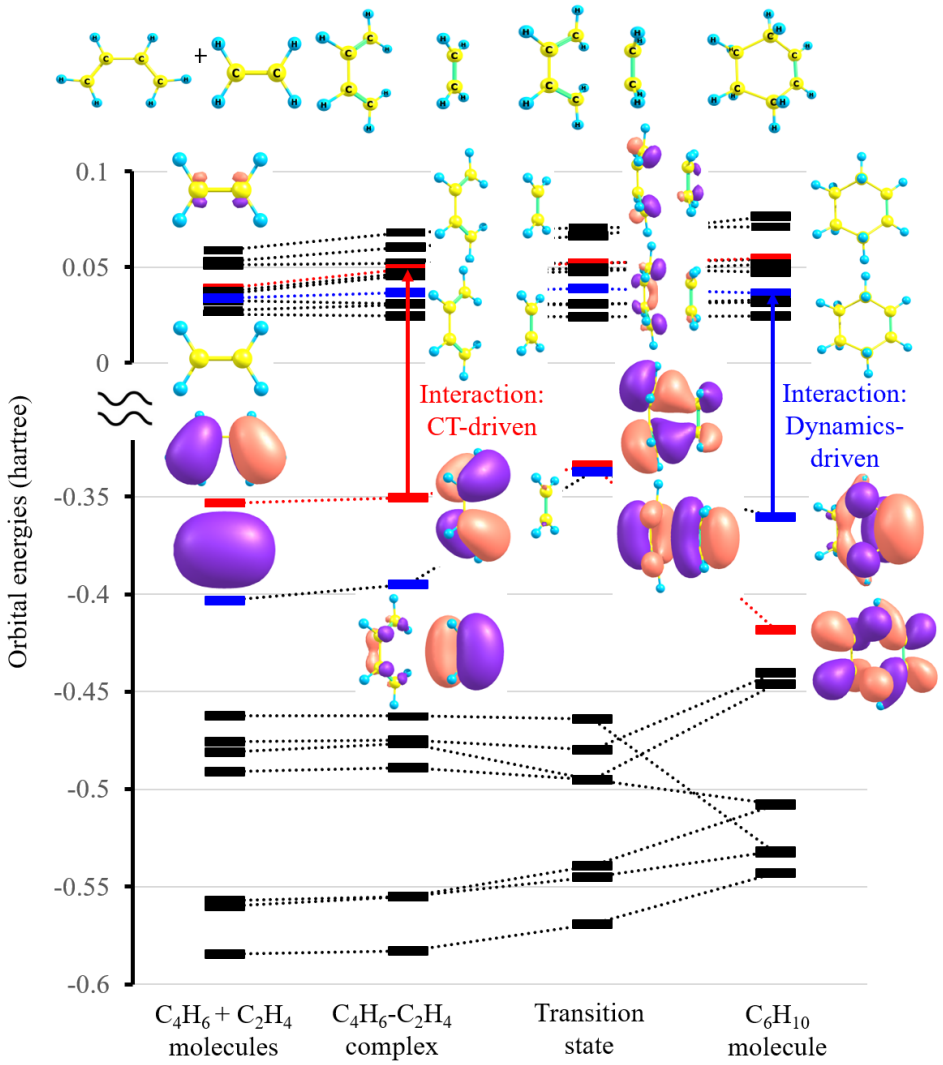


Reaction 36

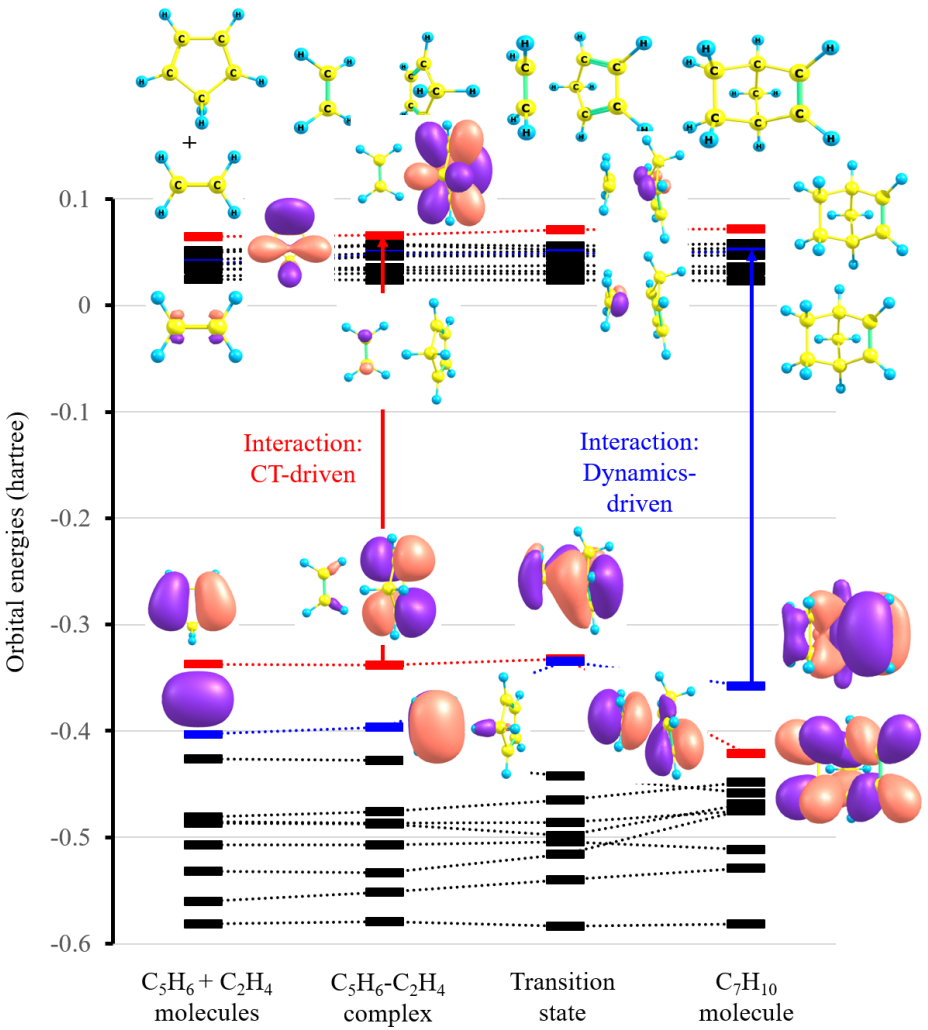



Reaction 37
Reaction 38
Orbital energies (hartree)
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
Interaction:
CT-driven
Interaction:
CT-driven
Interaction:
Dynamics-
driven
Interaction:
Dynamics-
driven
Cyclopentadiene
molecule
Transition
state
Cyclopentadien
molecule
1,5-Hexadiene
molecule
Transition
state
1,5-Hexadiene
molecule

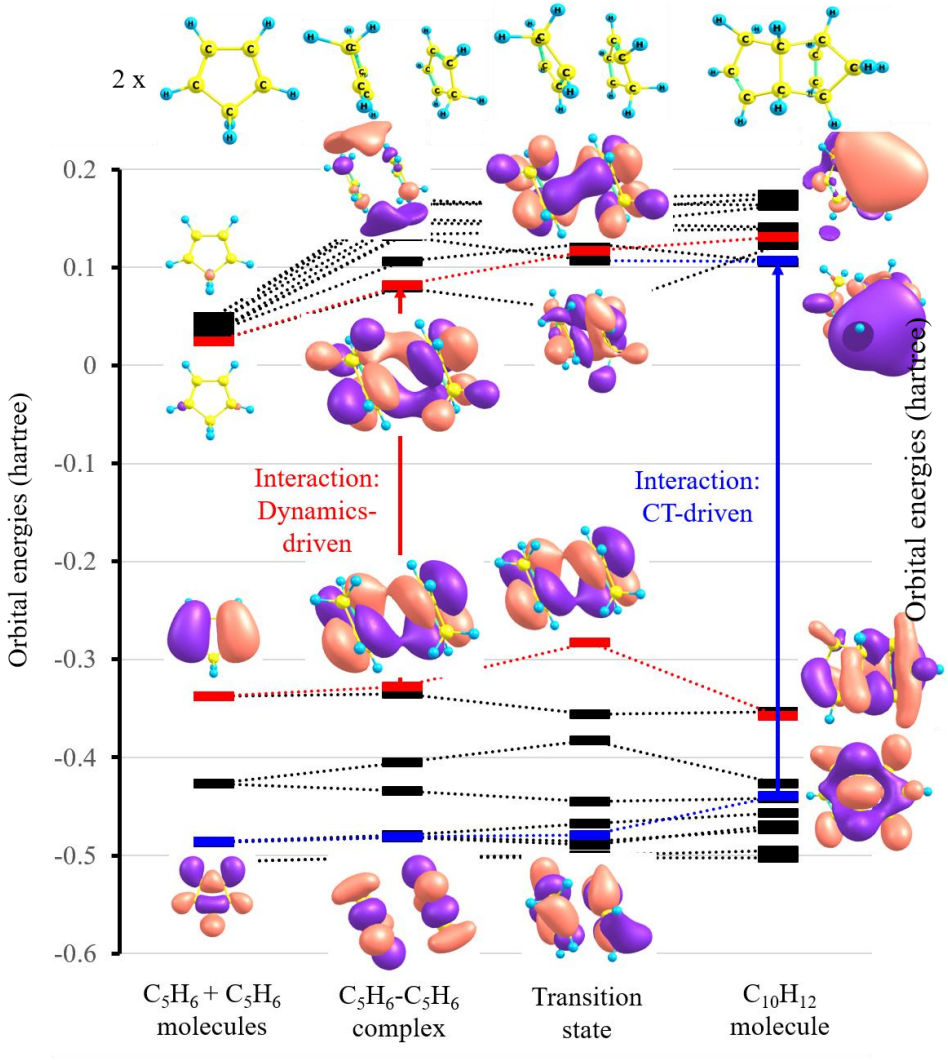
Reaction 39



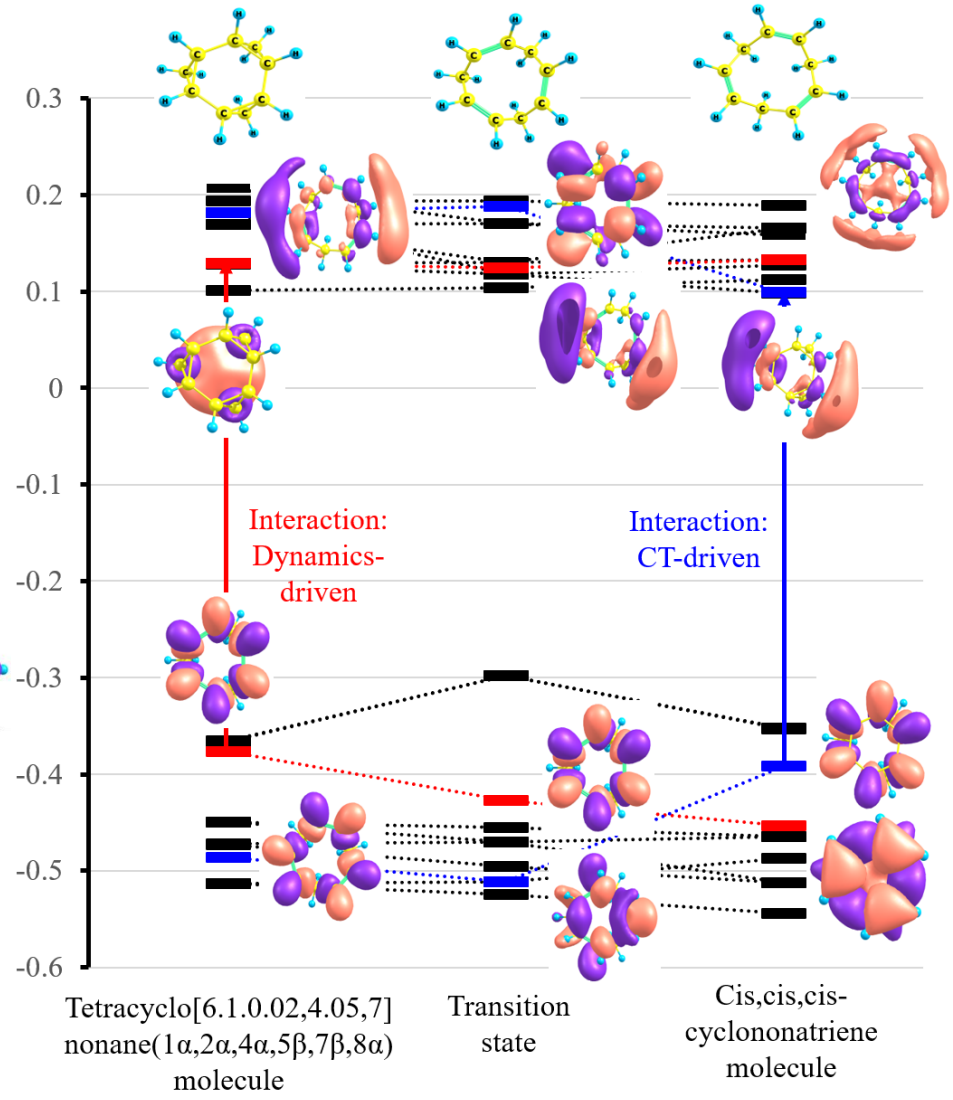
Reaction 40



Reaction 41



Reaction 42



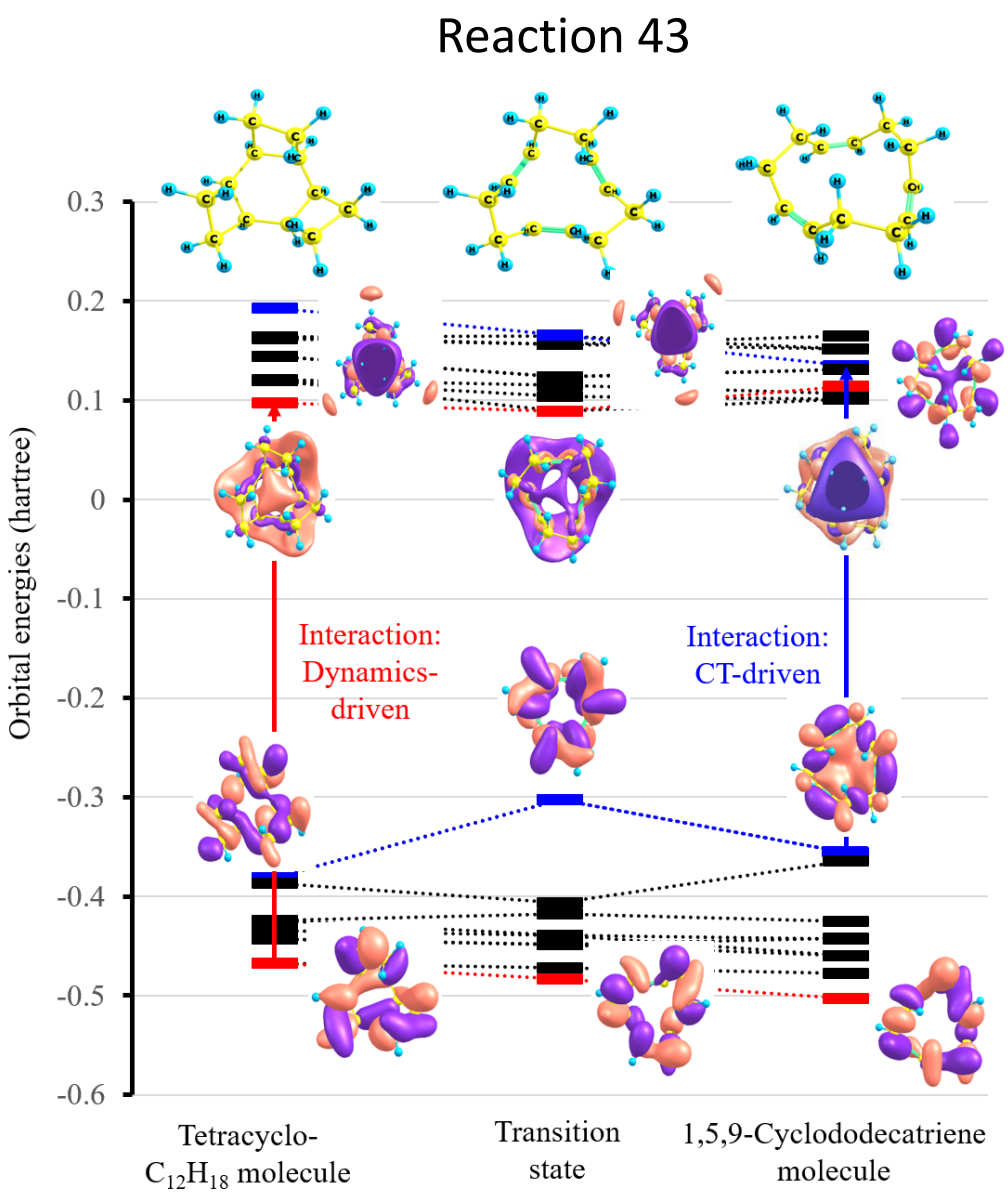

Reaction 43
Orbital energies (hartree)
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
Interaction: Dynamics-driven
Interaction: CT-driven
Tetracyclo-$C_{12}H_{18}$ molecule
Transition state
1,5,9-Cyclododecatriene molecule

Fig. S2. Mulliken populations of fundamental reactions. Reaction numbers correspond to those in Table 1. LC-BLYP+LRD/aug-cc-pVTZ calculations.

Reaction 1	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
H1	0.11475	0.00183	0.03214	-0.031	0	-0.00182	0
Cl1	-0.11292		-0.0631		-0.032144	-0.11192	0.001824
H2	-0.00183	-0.00183	0.031	0.031001		0.11374	

Reaction 2	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
O1	-0.242121	-0.024995	-0.2883	-0.08963	0.134349	-0.33898	-0.00947
H1	0.217126		0.19869			0.15938	
H2	0.215345	0.024995	0.22398	0.089632		0.17013	
H3	-0.19035		-0.1343		-0.134349	0.00947	0.00947

Reaction 3	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-1.028333	0.002897	-0.8607	-0.03222	-0.074326	-1.01518	-0.063711
H1	0.233592		0.26473			0.31984	

H2	0.231948		0.26124			0.31635	
H3	0.231513		0.2604			0.31529	
H4	0.334177		0.04211		0.074326	0.28974	0.06371
H5	-0.002897	-0.002897	0.03222	0.032216		-0.22603	

Reaction 4	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.242428		-0.3132			-0.38159	
H2	0.236648		0.22863		0.412813	0.31929	0.556068
H3	0.246965	0.806452	0.27067	0.739915		0.30182	
H4	0.236944		0.2267			0.31655	
H1	0.328323		0.3271			0.20623	
O1	-1.033374	-0.806452	-0.9061	-0.73991	-0.412812	-0.91956	-0.556069
H5	0.226922		0.16622			0.15726	

Reaction 5	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
O1	-0.573348	0.004621	-0.4599	-0.13628	-0.107019	-0.63794	0.016793

C1	-0.390184		-0.3772			-0.28442	
H1	0.137267		0.15257			0.16868	
H2	0.264502		0.27727			0.36872	
H3	0.30225		0.30031			0.40175	
H4	0.264134		-0.0293		0.107018	0.0036	-0.016793
H5	-0.004621	-0.004621	0.13627	0.136274		-0.0204	

Reaction 6	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
H1	0.224199	0.027241	0.13741	0.077076	0.137412	0.22368	0.223684
H2	-0.196958		-0.0603		-0.137412	-0.02664	-0.223684
H3	-0.02724	-0.02724	-0.0771	-0.07708		-0.19704	

Reaction 7	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
N1	-0.3966		-0.3503			-0.30365	
H1	0.183388	0.111092	0.17197	0.206945	-0.021825	0.1742	0.02917
H2	0.14738		0.15647			0.15862	

H3	0.176924		0.22877			0.18428	
O1	-0.316661	-0.111091	-0.3688	-0.20695	0.021825	-0.35345	-0.02917
H4	0.20557		0.1619			0.14	

Reaction 8	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-1.059815		-0.8588			-0.96534	
H1	0.297228		0.28271		-0.005031	0.31876	-0.003133
H2	0.203877	0.024202	0.28849	0.192957		0.32445	
H3	0.292261		0.28261			0.319	
H4	0.290651		0.19799		0.005031	0.20244	0.003132
Cl1	-0.024202	-0.024202	-0.193	-0.19296		-0.19931	

Reaction 9	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.63878		-0.6471			-0.60797	
C2	-0.710874	0.023345	-0.6215	0.15637	-0.210975	-0.62022	0.036
H1	0.264903		0.21718			0.23197	

H2	0.206689		0.22436			0.24243	
H3	0.207737		0.20945			0.19231	
H4	0.221472		0.21942			0.28745	
H5	0.214842		0.18725			0.31004	
H6	0.257356		0.36735			0.22132	
O1	-0.25695	-0.023345	-0.3257	-0.15637	0.210975	-0.40046	-0.036001
H7	0.233605		0.16931			0.14314	

Reaction 10	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken

Reaction 11	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.948344		-0.826			-1.00611	
H1	0.321326	0.007946	0.26172	-0.05222		0.26514	
H2	0.319048		0.25645		0.222204	0.24688	0.009109
H3	0.315916		0.25561			0.243	
H4	0.247954	-0.007947	0.27443	0.786495		0.26021	

O1	-0.255901		-0.2222		-0.222204	-0.00911	-0.009107

Reaction 12	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
P1	-0.104993		-0.1703			-0.02364	
H1	0.030354	0.007811	0.02069	0.005808	-0.129644	0.01089	-0.002521
H2	0.032893		0.01998			0.01023	
H3	0.049557		0.13545		0.129645	0.00453	0.002521
H4	-0.007812	-0.007812	-0.0058	-0.00581		-0.00201	

Reaction 13	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
O1	-0.234998	-0.016775	-0.1644	-0.04354	-0.164433	-0.04798	-0.047978
H1	0.218223		0.1209		0.164434	0.28219	0.047978
H2	0.016775	0.016775	0.04354	0.043537		-0.23421	

Reaction 14	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
H1	0.118153		0.12013		-0.156851	0.09871	0.000286
S1	-0.322642	0.001626	-0.277	-0.05236		-0.09843	
H2	0.206115		0.10449		0.156851	0.01458	-0.000287
H3	-0.001625	-0.001625	0.05236	0.05236		-0.01487	

Reaction 15	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
Cl1	0.061325	0.061325	-0.0752	-0.07525	0.08016	-0.11784	0.031584
H1	0.221775	-0.061325	0.15541	0.075247		0.14943	
O1	-0.2831		-0.0802		-0.08016	-0.03158	-0.031584

Reaction 16	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.962981	-0.018342	-0.8564	-0.11472	0.203342	-1.02879	0.017439

H1	0.313829		0.2506			0.27247	
H2	0.31135		0.24893			0.27188	
H3	0.31946		0.24214			0.20868	
H4	0.275519		0.31806			0.2932	
N1	-0.415446	0.018341	-0.3681	0.114723	-0.203341	-0.2456	-0.017438
H5	0.158268		0.16476			0.22817	

Reaction 17	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.556855		-0.6331			-0.65349	
C2	-0.63279		-0.5638			-0.67659	
H1	0.235163		0.21557			0.24851	
H2	0.235939	0.020414	0.21608	-0.14047	0.232558	0.21796	0.020468
H3	0.192924		0.20146			0.21276	
H4	0.27404		0.21307			0.20281	
H5	0.271993		0.2102			0.20636	
H6	0.252143		0.37303			0.26216	
N1	-0.407703	-0.020414	-0.3762	0.140473	-0.232558	-0.25529	-0.020468
H7	0.135146		0.14368			0.23482	

Reaction 18	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.556342		-0.6821			-0.66034	
C2	-0.632908		-0.5587			-0.68067	
H1	0.232252		0.21484			0.19417	
H2	0.229842	0.016893	0.214	-0.20046	0.199549	0.28348	0.011844
H3	0.198137		0.20012			0.20304	
H4	0.27418		0.20515			0.21345	
H5	0.271732		0.20622			0.21912	
H6	0.254456		0.40001			0.2396	
N1	-0.45909	-0.016892	-0.4137	0.200465	-0.199548	-0.37582	-0.011843
H7	0.091778		0.10741			0.16935	
H8	0.095964		0.10674			0.19463	

Reaction 19	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.998812	0.004559	-0.8734	0.158328	-0.168681	-0.95474	-0.018763
H1	0.230152		0.22543			0.31272	

H2	0.245583		0.25208			0.31194	
H3	0.243386		0.22721			0.31132	
H4	0.28425		0.32701			0.259	
N1	-0.378366		-0.4133		0.168681	-0.48489	0.018763
H5	0.186199	-0.004558	0.12841	-0.15833		0.12246	
H6	0.187609		0.12659			0.1222	

Reaction 20	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.697059		-0.5865			-0.83616	
C2	-0.378818		-0.1945			0.00663	
C3	-0.087888		-0.4418			-0.06258	
C4	0.02026		-0.1866			-0.39572	
C5	-0.907701		-0.6458			-0.75908	
H1	0.354415	0	0.27152	0	0	0.18656	0
H2	0.221852		0.2251			0.23417	
H3	0.215666		0.18026			0.24967	
H4	0.39564		0.43006			0.38678	
H5	0.252705		0.19016			0.21609	
H6	0.186633		0.27288			0.36004	

H7	0.196044		0.26585			0.20621	
H8	0.228251		0.21932			0.20738	

Reaction 21	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken

Reaction 22	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
H1	0.304986	0.000699	0.12529	-0.12432	-0.124319	-0.00071	-0.304064
F1	-0.304287		-0.2496		-0.125288	-0.30336	0.000707
H2	-0.000699	-0.000699	0.12432	0.124319		0.30406	

Reaction 23	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
H1	-0.002529	-0.002529	0.01839	0.018389	-0.408143	0.29895	0.000815
F1	-0.321809	0.00253	-0.4265	-0.01839		-0.29813	

C1	-0.421249		-0.463			-1.00062	
H2	0.255958		0.29271		0.408143	0.33563	-0.000816
H3	0.2378		0.29196			0.33268	
H4	0.25183		0.28649			0.33149	

Reaction 24	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
F1	-0.448584		-0.7211		-0.721122	-0.97035	-0.721122
C1	-0.441452		-0.4887			-0.44494	
H1	0.289653	-0.029384	0.31433	-0.27815		0.29187	
H2	0.285677		0.3081		-0.278878	0.2872	-0.278878
H3	0.285322		0.30927			0.28699	
F2	-0.970615	-0.970615	-0.7218	-0.72185		-0.45076	

Reaction 25	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
F1	-0.961657	-0.714551	-0.8059	-0.43204	-0.805902	-0.42525	-0.42525
C1	-0.624892		-0.643		-0.194098	-0.46159	-0.57475

H1	0.293821		0.34204			0.29431	
H2	0.289162		0.33787			0.28975	
H3	0.289015		0.33695			0.28878	
Cl1	-0.285448	-0.285448	-0.568	-0.56796		-0.986	

Reaction 26	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
F1	-0.781928	-0.781928	-0.6807	-0.68071		-0.44611	
C1	-0.645008		-0.558			-0.42574	
H1	0.219034		0.30699		-0.289844	0.28663	-0.026576
H2	0.217083	-0.218073	0.32056	-0.3193		0.27928	
H3	0.294522		0.32132			0.27937	
O1	-0.58195		-0.7532		-0.710157	-0.98725	-0.973424
H4	0.278246		0.04301			0.01382	

Reaction 27	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
Cl1	-0.965798	-0.745179	-0.6627	-0.33471	-0.662715	-0.25091	-0.250912

C1	-0.612005		-0.7546			-0.61372	
H1	0.278357		0.35904			0.2802	
H2	0.272659		0.36324		-0.337286	0.27193	-0.749088
H3	0.281608		0.36032			0.27903	
Cl2	-0.254822	-0.254822	-0.6653	-0.66529		-0.96653	

Reaction 28	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
N1	-0.119637		-0.1224		-0.072961	-0.0059	-0.001253
N2	-0.095585	0	0.04941	0		0.00465	
H1	0.215222		0.07296		0.072961	0.00125	0.001254

Reaction 29	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
H1	0.384692		0.02042		0.02042	-0.00106	-0.001059
C1	-0.157217	0	0.08074	0	-0.020419	0.08016	0.001058
O1	-0.227476		-0.1012			-0.0791	

Reaction 30	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
H1	-0.000479	-0.000479	-0.0271	-0.02707		0.22264	
C1	-0.684937		-0.5304			-0.56852	
C2	-0.686813		-0.7775			-0.71851	
H2	0.353812	0.000479	0.34336	0.02707	0	0.21936	0
H3	0.342756		0.3327			0.21882	
H4	0.343347		0.3345			0.31897	
H5	0.332314		0.32449			0.30723	

Reaction 31	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.636333		-0.4446			-0.07203	
C2	-0.693674		-0.8184			-0.76236	
H1	0.344376	-0.000625	0.35364	0.01569	0	0.18055	0
H2	0.330085		0.34144			0.17461	
H3	0.334106		0.29655			0.2902	
H4	0.320815		0.2871			0.29127	

C3	-1.030754	0.000625	-0.9262	-0.01569		-0.76899	
H5	0.315972		0.30475			0.17951	
H6	0.358241		0.30311			0.24563	
H7	0.357166		0.30269			0.24163	

Reaction 32	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.345626	-0.624952	-0.3175	-0.47532	0	-0.37602	0
N1	-0.279326		-0.1578			0.11402	
H1	0.624952	0.624952	0.47532	0.475317		0.262	

Reaction 33	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
H1	0.261538	0	0.32253	0	0	0.39848	0
C1	-0.377204		-0.5129			-0.85622	
C2	-0.411424		-0.5258			-0.86228	
C3	-0.472647		-0.4325			0.02054	
C4	-0.474868		-0.4307			0.02746	

H2	0.247059	0.30611	0.39697
H3	0.393697	0.37965	0.25646
H4	0.222577	0.25497	0.17269
H5	0.223986	0.26204	0.18526
H6	0.387285	0.37663	0.26064

Reaction 34	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.797844	0	-0.4238	0	0	-0.16978	0
C2	-0.045888		-0.3136			-0.36925	
C3	-0.186076		-0.3687			-0.49251	
C4	-0.181321		-0.3838			-0.51994	
C5	-0.033329		-0.2825			-0.34264	
C6	-0.873664		-0.4965			-0.2862	
H1	0.163011		0.23475			0.25004	
H2	0.335097		0.34599			0.44843	
H3	0.365891		0.34386			0.46054	
H4	0.148728		0.23275			0.24355	
H5	0.375253		0.31907			0.19723	
H6	0.180405		0.2424			0.19687	

H7	0.370233		0.31507			0.19044	
H8	0.179504		0.23512			0.19321	

Reaction 35	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
H1	0.270513		0.30262			0.32554	
C1	-0.495988		-0.6017			-0.69928	
C2	-0.463552		-0.6216			-0.79398	
C3	1.400859		0.82835			0.50261	
C4	-0.593208		-0.4638			-0.35808	
C5	-0.567066		-0.424			-0.32841	
C6	1.464194		0.88653			0.56178	
C7	-1.43413	0	-0.9046	0	0	-0.56143	0
H2	0.307918		0.31973			0.37166	
H3	0.314773		0.32337			0.34583	
H4	0.220862		0.25697			0.19588	
H5	0.209892		0.28623			0.31556	
H6	0.223265		0.25291			0.19371	
H7	0.267736		0.2351			0.24493	
H8	0.283069		0.237			0.25288	

C8	-1.409137		-0.9131			-0.5692	

Reaction 36	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.834439		-0.5853			-0.69624	
C2	-0.740184		-0.6246			-0.88051	
C3	0.000801		-0.2004			-0.3931	
C4	-0.369853		-0.1755			0.02114	
C5	-0.099629		-0.4574			-0.09858	
H1	0.204435		0.26456			0.2005	
H2	0.362305	0	0.27061	0	0	0.18946	0
H3	0.187878		0.27396			0.36473	
H4	0.205559		0.22102			0.22612	
H5	0.230293		0.21736			0.21053	
H6	0.213394		0.18937			0.25476	
H7	0.256854		0.18501			0.2161	
H8	0.382586		0.42138			0.38508	

Reaction 37	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.322811		-0.2114			-0.16303	
C2	-0.200916		-0.2468			-0.38622	
C3	-0.546298		-0.5777			-0.38652	
C4	-0.389531		-0.5734			-0.51915	
C5	-0.509815		-0.644			-0.51807	
H1	0.250932	0	0.34297	0	0	0.25119	0
H2	0.323428		0.36799			0.2327	
H3	0.233692		0.37608			0.33082	
H4	0.416926		0.37794			0.33391	
H5	0.333338		0.37576			0.41584	
H6	0.411055		0.41258			0.40852	

Reaction 38	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	0.15823	0	-0.2607	0	0	0.19238	0
C2	0.140639		-0.28			0.09775	

C3	-0.949428	-0.5283	-0.10578
C4	-0.107864	-0.5169	-0.96013
C5	-0.130753	-0.5411	-0.97601
C6	-0.963572	-0.5289	-0.11694
H1	0.431936	0.31126	0.19917
H2	0.19863	0.30709	0.48485
H3	0.093631	0.2516	0.11067
H4	0.108353	0.25433	0.06295
H5	0.100019	0.24575	0.02807
H6	0.083042	0.24809	0.10542
H7	0.195825	0.30545	0.48279
H8	0.431265	0.30254	0.19104
H9	0.096397	0.21298	0.07951
H10	0.113651	0.21677	0.12426

Reaction 39	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.655611		-0.5414			-0.31125	
H1	0.321904	0.002855	0.30802	0.023879	0	0.19439	0
H2	0.368365		0.29873			0.13479	

C2	-0.723341		-0.657			-0.38849	
H3	0.321872		0.30621			0.20089	
H4	0.369666		0.30936			0.14421	
C3	-0.708142		-0.5062			-0.12909	
H5	0.291848		0.25832			0.12121	
H6	0.280194		0.32445			0.17588	
C4	-0.21168		-0.3703			-0.54322	
H7	0.353971	-0.002858	0.31585	-0.02388		0.39659	
C5	-0.154429		-0.3624			-0.54435	
H8	0.36611		0.33053			0.43651	
C6	-0.76626		-0.5791			-0.17205	
H9	0.269185		0.32362			0.17086	
H10	0.276345		0.24135			0.11311	

Reaction 40	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.152697		-0.3221			-0.45408	
H1	0.302891	-0.000512	0.25084	0.104827	0	0.2278	0
H2	0.203106		0.14644			0.19083	
C2	-0.293341		-0.2793			-0.17744	

C3	-0.30677		-0.2849			-0.1804	
C4	-0.586631		-0.5745			-0.59162	
C5	-0.597112		-0.5897			-0.61782	
H3	0.325406		0.44078			0.36386	
H4	0.327763		0.44415			0.3726	
H5	0.390166		0.43927			0.49207	
H6	0.386707		0.43394			0.46708	
C6	-0.722331		-0.6359			-0.44573	
C7	-0.734448		-0.6455			-0.44318	
H7	0.250245	0.00051	0.25399	-0.10483		0.14705	
H8	0.245108		0.2464			0.12449	
H9	0.483051		0.3383			0.25651	
H10	0.478885		0.33785			0.26799	

Reaction 41	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
H1	0.111836		0.11497			0.10806	
C1	-0.174732	0.000122	-0.2177	-0.00034	0	-0.23963	0
C2	-0.168687		-0.1413			-0.02981	
C3	-0.151414		-0.1682			-0.18611	

C4	-0.154069		-0.2115		-0.21721
C5	-0.171171		-0.0941		-0.03123
H2	0.13192		0.1318		0.10842
H3	0.139023		0.14022		0.101
H4	0.142658		0.13924		0.14135
H5	0.1478		0.15579		0.14862
H6	0.146958		0.15042		0.10126
C6	-0.152823		-0.1837		-0.08935
C7	-0.171213		-0.1234		-0.10499
H7	0.147111		0.16172		0.135
H8	0.147797		0.1675		0.13535
C8	-0.152382		-0.1644		-0.20801
C9	-0.167937	-0.000122	-0.1473	0.000336	-0.113
H9	0.142706		0.13607		0.13104
H10	0.139013		0.13444		0.13035
C10	-0.175893		-0.2237		-0.24533
H11	0.111686		0.11302		0.10821
H12	0.131813		0.1301		0.116

Reaction 42	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
H1	0.112075		0.13202			0.12392	
C1	-0.069128		-0.1286			-0.12196	
C2	-0.303815		-0.2316			-0.24543	
C3	-0.305133		-0.2331			-0.24684	
H2	0.1117		0.13198			0.12369	
H3	0.104986		0.11179			0.11749	
H4	0.117957		0.1174			0.12846	
C4	-0.072068		-0.1306			-0.12315	
C5	-0.070001	0	-0.1301	0	0	-0.12429	0
H5	0.111912		0.13199			0.12367	
C6	-0.069737		-0.1296			-0.12268	
H6	0.117959		0.11744			0.12863	
C7	-0.305032		-0.2326			-0.24609	
H7	0.111737		0.13177			0.12372	
H8	0.105326		0.11168			0.11729	
H9	0.118173		0.11745			0.12857	
C8	-0.072509		-0.1316			-0.12517	
H10	0.111798		0.13155			0.12356	

H11	0.105087	0.11181	0.11739
C9	-0.07297	-0.1307	-0.12419
H12	0.111684	0.13156	0.12343

Reaction 43	Reactant	Mulliken	TS	Mulliken forward	Mulliken backward	Product	Mulliken
C1	-0.285076		-0.2416			-0.22759	
C2	-0.258915		-0.228			-0.24804	
H1	0.118642		0.1206			0.13262	
H2	0.117276		0.11633			0.11794	
H3	0.123262		0.11115			0.11207	
H4	0.12311		0.1188			0.13242	
C3	-0.105819	0	-0.147	0	0	-0.11785	0
C4	-0.0746		-0.1327			-0.14637	
H5	0.117013		0.1322			0.12299	
C5	-0.10566		-0.1484			-0.11859	
H6	0.126305		0.15269			0.12331	
C6	-0.075133		-0.1343			-0.14705	
C7	-0.258896		-0.2284			-0.2481	
C8	-0.287312		-0.2425			-0.22867	

H7	0.118831	0.12035	0.13244
H8	0.117082	0.13213	0.12314
H9	0.117411	0.11647	0.11794
H10	0.123868	0.11134	0.11169
H11	0.123173	0.11891	0.13246
C9	-0.105999	-0.1478	-0.118
C10	-0.075394	-0.1341	-0.14646
H12	0.126379	0.15277	0.12334
H13	0.116974	0.13209	0.12308
C11	-0.258271	-0.2276	-0.24798
H14	0.118748	0.1205	0.13241
C12	-0.287756	-0.2434	-0.22894
H15	0.123023	0.11898	0.13258
H16	0.126379	0.15284	0.12346
H17	0.124008	0.11124	0.11174
H18	0.117345	0.11629	0.11801

Fig. S3. Charge transfer (CT) directions in the processes from the reactants to the TSs in Mulliken populations and in the initial processes of the reactive orbital energy diagrams (ROED) of fundamental reactions and their differences. Reaction numbers correspond to those in Table 1. LC-BLYP+LRD/aug-cc-pVTZ calculations.

Reaction	CT in Mulliken			CT in ROED			Mulliken vs ROED
	Donor		Acceptor	Donor		Acceptor	
Reaction 1	Forward			Forward			
	H	→	HCl	H	→	HCl	Same
	Backward			Backward			
	H	→	HCl	H	→	HCl	Same
Reaction 2	Forward			Forward			
	H_2	→	OH	OH	→	H_2	Opposite
	Backward			Backward			
	H_2O	→	H	H_2O	→	H	Same
Reaction 3	Forward			Forward			
	H	→	CH_4	CH_4	→	H	Opposite

	Backward H_2	$\rightarrow CH_3$	Backward CH_3	$\rightarrow H_2$	Opposite
Reaction 4	Forward OH	$\rightarrow CH_4$	Forward OH	$\rightarrow CH_4$	Same
	Backward H_2O	$\rightarrow CH_3$	Backward H_2O	$\rightarrow CH_3$	Same
Reaction 5	Forward H	$\rightarrow CH_3OH$	Forward CH_3OH	$\rightarrow H$	Opposite
	Backward H_2	$\rightarrow CH_2OH$	Backward CH_2OH	$\rightarrow H_2$	Opposite
Reaction 6	Forward H_2	$\rightarrow H$	Forward H_2	$\rightarrow H$	Same
	Backward H_2	$\rightarrow H$	Backward H_2	$\rightarrow H$	Same
Reaction 7	Forward NH_3	$\rightarrow$ OH	Forward NH_3	$\rightarrow$ OH	Same

	Backward		Backward		
	H_2O	→ NH_2	H_2O	→ NH_2	Same
Reaction 8	Forward		Forward		
	CH_4	→ Cl	CH_4	→ Cl	Same
	Backward		Backward		
	HCl	→ CH_3	CH_3	→ HCl	Opposite
Reaction 9	Forward		Forward		
	C_2H_6	→ OH	OH	→ C_2H_6	Opposite
	Backward		Backward		
	H_2O	→ C_2H_5	H_2O	→ C_2H_5	Same
Reaction 10	No TS		No TS		
Reaction 11	Forward		Forward		
	OH	→ CH_3	OH	→ CH_3	Same
	Backward		Backward		
	CH_4	→ O	CH_4	→ O	Same
Reaction 12	Forward		Forward		

	H	→ PH_3	H	→ PH_3	Same
	Backward		Backward		
	H_2	→ PH_2	H_2	→ PH_2	Same
Reaction 13	Forward		Forward		
	H	→ OH	H	→ OH	Same
	Backward		Backward		
	H_2	→ O	H_2	→ O	Same
Reaction 14	Forward		Forward		
	SH_2	→ H	SH_2	→ H	Same
	Backward		Backward		
	H_2	→ SH	H_2	→ SH	Same
Reaction 15	Forward		Forward		
	OH	→ Cl	OH	→ Cl	Same
	Backward		Backward		
	HCl	→ O	HCl	→ O	Same
Reaction 16	Forward		Forward		

	NH_2	→ CH_3	CH_3	→ NH_2	Opposite
	Backward		Backward		
	CH_4	→ NH	CH_4	→ NH	Same
Reaction 17	Forward		Forward		
	NH_2	→ C_2H_5	C_2H_5	→ NH_2	Opposite
	Backward		Backward		
	C_2H_6	→ NH	C_2H_6	→ NH	Same
Reaction 18	Forward		Forward		
	NH_3	→ C_2H_5	NH_3	→ C_2H_5	Same
	Backward		Backward		
	C_2H_6	→ NH_2	C_2H_6	→ NH_2	Same
Reaction 19	Forward		Forward		
	CH_4	→ NH_2	CH_4	→ NH_2	Same
	Backward		Backward		
	NH_3	→ CH_3	NH_3	→ CH_3	Same
Reaction 20	Intramolecular CT		Intramolecular CT		

Reaction 21	No TS		No TS		
Reaction 22	Forward H Backward H	→ HF → HF	Forward H Backward H	→ HF → HF	Same Same
Reaction 23	Forward H Backward CH_3	→ CH_3F → HF	Forward H Backward HF	→ CH_3F → CH_3	Same Opposite
Reaction 24	Forward F- Backward F-	→ CH_3F → CH_3F	Forward F- Backward F-	→ CH_3F → CH_3F	Same Same
Reaction 25	Forward FCH_3 Backward	→ Cl^-	Forward FCH_3 Backward	→ Cl^-	Same

	$ClCH_3$	→ F^-	$ClCH_3$	→ F^-	Same
Reaction 26	Forward F^- Backward	→ CH_3OH	Forward F^- Backward	→ CH_3OH	Same
	OH^-	→ CH_3F	OH^-	→ CH_3F	Same
Reaction 27	Forward CH_3Cl Backward	→ Cl	Forward CH_3Cl Backward	→ Cl	Same
	CH_3Cl	→ Cl	CH_3Cl	→ Cl	Same
Reaction 28	Forward Intramolecular CT Backward		Forward Intramolecular CT Backward		
	H	→ N_2	N_2	→ H	Opposite
Reaction 29	Forward Intramolecular CT Backward		Forward Intramolecular CT Backward		

	H	→ CO	CO	→ H	Opposite
Reaction 30	Forward C_2H_4 → H Backward Intramolecular CT		Forward C_2H_4 → H Backward Intramolecular CT		Same
Reaction 31	Forward C_2H_4 → CH_3 Backward Intramolecular CT		Forward C_2H_4 → CH_3 Backward Intramolecular CT		Same
Reaction 32	Forward CN → H Backward Intramolecular CT		Forward CN → H Backward Intramolecular CT		
Reaction 33	Intramolecular CT		Intramolecular CT		
Reaction 34	Intramolecular CT		Intramolecular CT		
Reaction 35	Intramolecular CT		Intramolecular CT		

Reaction 36	Intramolecular CT	Intramolecular CT	
Reaction 37	Intramolecular CT	Intramolecular CT	
Reaction 38	Intramolecular CT	Intramolecular CT	
Reaction 39	Forward $C_2H_4 \rightarrow C_4H_6$ Backward Intramolecular CT	Forward $C_4H_6 \rightarrow C_2H_4$ Backward Intramolecular CT	Opposite
Reaction 40	Forward $C_5H_6 \rightarrow C_2H_4$ Backward Intramolecular CT	Forward $C_5H_6 \rightarrow C_2H_4$ Backward Intramolecular CT	Same
Reaction 41	Forward $C_5H_6 \rightarrow C_5H_6$ Backward Intramolecular CT	Forward $C_5H_6 \rightarrow C_5H_6$ Backward Intramolecular CT	Same
Reaction 42	Intramolecular CT	Intramolecular CT	

Reaction 43	Intramolecular CT	Intramolecular CT