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ELECTRONIC SUPPLEMENTARY INFORMATION

Rethinking the $X^- + CH_3Y$ [X = OH, SH, CN, NH_2, PH_2; Y = F, Cl, Br, I] S_N2 reactions

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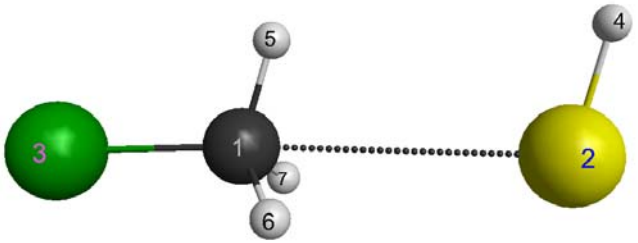
Content

Energies, structures, and frequencies for the stationary points of the potential energy surface of the $SH^- + CH_3Y$ [Y = F, Cl, Br, I] S_N2 reactions obtained at different levels of theory

Table S1. Energies, structures, and frequencies for the PreMIN [Y = F, Cl, Br, I] ion-dipole complexes (C_s symmetry) obtained at different levels of theory

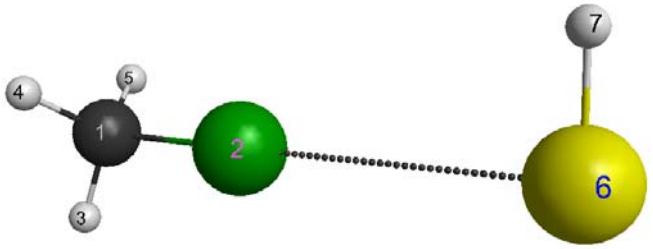


1	C							
2	S	1	r_1					
3	Y	1	r_2	2	a_1			
4	H	2	r_3	1	a_2	3	180.0	
5	H	1	r_4	3	a_3	2	180.0	
6	H	1	r_5	3	a_4	5	d_1	
7	H	1	r_5	3	a_4	5	$-d_1$	

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	**$FCH_3\cdots SH^-$**	**$ClCH_3\cdots SH^-$**	**$BrCH_3\cdots SH^-$**	**$ICH_3\cdots SH^-$**	**$FCH_3\cdots SH^-$**	**$ClCH_3\cdots SH^-$**	**$BrCH_3\cdots SH^-$**	**$ICH_3\cdots SH^-$**	**$FCH_3\cdots SH^-$**	**$ClCH_3\cdots SH^-$**	**$BrCH_3\cdots SH^-$**	**$ICH_3\cdots SH^-$**
Energy [E_h]	−537.725620	−897.735692	−853.700248	−732.845529	−537.967011	−897.947349	−853.908314	−733.048753	−538.012500	−898.002706	−853.966126	−733.097495
r_1 [Å]	3.328	3.274	3.229	3.173	3.348	3.299	3.230	3.180	3.356	3.301	3.233	3.178
r_2 [Å]	1.441	1.839	1.996	2.213	1.411	1.813	1.986	2.197	1.412	1.820	1.989	2.199
r_3 [Å]	1.355	1.355	1.355	1.356	1.347	1.347	1.347	1.347	1.345	1.345	1.345	1.346
r_4 [Å]	1.095	1.093	1.092	1.093	1.088	1.084	1.083	1.082	1.086	1.082	1.081	1.081
r_5 [Å]	1.094	1.092	1.092	1.092	1.087	1.084	1.082	1.082	1.085	1.082	1.081	1.081
a_1 [deg]	175.8	176.8	177.1	177.1	176.9	176.5	177.3	178.5	176.9	177.5	177.3	178.5
a_2 [deg]	109.5	103.2	100.2	96.9	104.5	98.1	96.2	92.4	105.2	99.3	96.4	93.5
a_3 [deg]	108.3	108.0	107.4	106.9	109.0	108.6	107.5	106.9	108.9	108.3	107.2	106.7
a_4 [deg]	108.5	108.1	107.6	107.1	109.1	108.8	107.7	107.3	109.0	108.4	107.4	107.0
d_1 [deg]	119.9	119.8	119.8	119.8	119.9	119.9	119.8	119.8	119.9	119.8	119.8	119.8
ZPE [cm^{-1}]	10180	9516	9673	9551	10118	9728	9605	9491	10106	9738	9596	9476
ω_1 [cm^{-1}]	40	46	47	58	30	6*i*	35*i*	41	42*i*	32*i*	32*i*	21
ω_2 [cm^{-1}]	58	61	64	70	54	56	72	72	55	54	62	69
ω_3 [cm^{-1}]	103	84	82	83	95	62	80	78	92	72	71	72
ω_4 [cm^{-1}]	108	104	97	96	104	101	96	95	101	98	93	92
ω_5 [cm^{-1}]	134	125	136	160	128	118	140	155	123	111	128	151
ω_6 [cm^{-1}]	933	638	521	439	983	644	517	431	977	644	513	427
ω_7 [cm^{-1}]	1142	990	928	862	1160	996	929	859	1159	992	925	859
ω_8 [cm^{-1}]	1143	992	930	866	1161	1005	929	862	1160	994	929	862
ω_9 [cm^{-1}]	1412	1299	1249	1190	1433	1322	1261	1202	1436	1327	1265	1204
ω_{10} [cm^{-1}]	1473	1446	1436	1426	1489	1466	1456	1447	1492	1473	1461	1451
ω_{11} [cm^{-1}]	1476	1450	1440	1429	1492	1470	1459	1450	1496	1476	1465	1454
ω_{12} [cm^{-1}]	2705	2703	2704	2702	2658	2657	2657	2657	2656	2655	2654	2654
ω_{13} [cm^{-1}]	3126	3141	3143	3143	3080	3110	3121	3124	3085	3115	3123	3124
ω_{14} [cm^{-1}]	3251	3274	3282	3286	3181	3221	3244	3252	3188	3230	3248	3253
ω_{15} [cm^{-1}]	3256	3278	3287	3293	3187	3227	3249	3257	3193	3234	3254	3258

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

Table S2. Energies, structures, and frequencies for the FSMIN [Y = Cl, Br, I] front-side complexes (C_s symmetry) obtained at different levels of theory

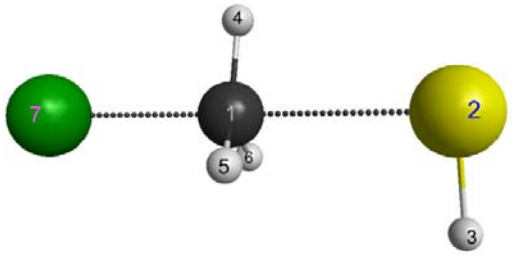


1	C						
2	Y	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_3	2	a_2	3	d_1
5	H	1	r_3	2	a_2	3	$-d_1$
6	S	2	r_4	1	a_3	3	0.0
7	H	6	r_5	2	a_4	3	180.0

Level[a]	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
System	$CH_3Cl\cdots SH^-$	$CH_3Br\cdots SH^-$	$CH_3I\cdots SH^-$	$CH_3Cl\cdots SH^-$	$CH_3Br\cdots SH^-$	$CH_3I\cdots SH^-$	$CH_3Cl\cdots SH^-$	$CH_3Br\cdots SH^-$	$CH_3I\cdots SH^-$
Energy [E_h]	−897.716710	−853.688208	−732.843994	−897.930382	−853.896686	−733.047610	−897.985265	−853.954773	−733.097001
r_1 [Å]	1.795	1.976	2.226	1.769	1.968	2.212	1.780	1.969	2.214
r_2 [Å]	1.099	1.099	1.100	1.090	1.089	1.090	1.088	1.087	1.088
r_3 [Å]	1.099	1.099	1.100	1.090	1.089	1.090	1.088	1.087	1.088
r_4 [Å]	3.512	3.193	3.101	3.601	3.163	3.057	3.479	3.153	3.045
r_5 [Å]	1.356	1.356	1.355	1.347	1.347	1.346	1.346	1.345	1.344
a_1 [deg]	109.1	109.0	109.0	109.6	108.9	108.9	109.3	108.7	108.7
a_2 [deg]	109.2	109.0	109.0	109.5	109.0	109.0	109.3	108.8	108.8
a_3 [deg]	177.5	179.6	179.6	185.2	180.2	180.0	180.6	180.1	180.0
a_4 [deg]	102.4	93.5	92.8	73.5	91.2	92.1	88.8	91.2	92.0
d_1 [deg]	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
ZPE [cm^{-1}]	9742	9620	9491	9709	9601	9469	9703	9584	9443
ω_1 [cm^{-1}]	12*i*	4*i*	13*i*	37*i*	43	54	47*i*	7*i*	39*i*
ω_2 [cm^{-1}]	39	81	97	27	73	96	41	83	100
ω_3 [cm^{-1}]	60	91	103	40	93	102	60	91	105
ω_4 [cm^{-1}]	68	94	126	59	96	128	70	95	130
ω_5 [cm^{-1}]	107	217	332	111	231	336	102	221	332
ω_6 [cm^{-1}]	744	575	467	755	572	465	743	570	463
ω_7 [cm^{-1}]	1015	918	811	1049	920	808	1021	919	805
ω_8 [cm^{-1}]	1015	918	811	1050	921	809	1021	919	805
ω_9 [cm^{-1}]	1351	1281	1204	1381	1295	1213	1374	1293	1209
ω_{10} [cm^{-1}]	1472	1460	1449	1489	1479	1468	1495	1484	1471
ω_{11} [cm^{-1}]	1472	1460	1450	1489	1479	1469	1496	1484	1472
ω_{12} [cm^{-1}]	2698	2704	2712	2655	2661	2671	2652	2658	2669
ω_{13} [cm^{-1}]	3076	3072	3064	3047	3049	3040	3051	3052	3041
ω_{14} [cm^{-1}]	3183	3184	3179	3134	3145	3140	3140	3150	3142
ω_{15} [cm^{-1}]	3184	3184	3179	3134	3146	3140	3140	3150	3142

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

Table S3. Energies, structures, and frequencies for the WaldenTS [Y = F, Cl, Br, I] transition states (C_s symmetry) obtained at different levels of theory

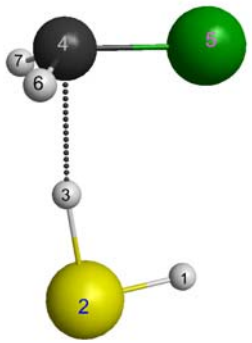


1	C						
2	S	1	r_1				
3	H	2	r_2	1	a_1		
4	H	1	r_3	2	a_2	3	180.0
5	H	1	r_4	4	a_3	2	d_1
6	H	1	r_4	4	a_3	2	$-d_1$
7	Y	1	r_5	4	a_4	2	180.0

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	**[F·CH$_3$·SH]$^-$**	**[Cl·CH$_3$·SH]$^-$**	**[Br·CH$_3$·SH]$^-$**	**[I·CH$_3$·SH]$^-$**	**[F·CH$_3$·SH]$^-$**	**[Cl·CH$_3$·SH]$^-$**	**[Br·CH$_3$·SH]$^-$**	**[I·CH$_3$·SH]$^-$**	**[F·CH$_3$·SH]$^-$**	**[Cl·CH$_3$·SH]$^-$**	**[Br·CH$_3$·SH]$^-$**	**[I·CH$_3$·SH]$^-$**
Energy [E_h]	−537.693051	−897.722935	−853.692326	−732.841483	−537.930333	−897.932966	−853.900664	−733.044877	−537.976405	−897.988946	−853.958888	−733.093890
r_1 [Å]	2.311	2.524	2.572	2.635	2.308	2.520	2.580	2.649	2.307	2.518	2.580	2.649
r_2 [Å]	1.353	1.354	1.354	1.354	1.344	1.345	1.346	1.346	1.343	1.344	1.344	1.344
r_3 [Å]	1.084	1.084	1.085	1.086	1.074	1.074	1.074	1.075	1.072	1.072	1.073	1.074
r_4 [Å]	1.082	1.083	1.083	1.085	1.072	1.073	1.073	1.075	1.070	1.071	1.072	1.073
r_5 [Å]	1.901	2.203	2.310	2.468	1.896	2.205	2.307	2.461	1.899	2.205	2.306	2.460
a_1 [deg]	95.2	93.2	92.4	91.3	95.1	92.6	91.7	90.6	95.2	92.9	92.1	91.1
a_2 [deg]	90.3	85.1	84.0	82.6	90.6	85.6	84.2	82.8	90.6	85.4	84.1	82.6
a_3 [deg]	119.5	119.1	118.7	118.0	119.5	119.1	118.6	118.0	119.5	119.1	118.7	118.0
a_4 [deg]	88.8	94.6	95.9	97.5	88.7	94.4	96.0	97.7	88.6	94.4	96.0	97.7
d_1 [deg]	92.4	82.4	80.2	77.4	92.6	82.6	80.0	77.1	92.7	82.6	80.0	77.1
ZPE [cm^{-1}]	10066	9809	9688	9564	9968	9724	9614	9488	9958	9710	9592	9486
ω_1 [cm^{-1}]	566*i*	489*i*	436*i*	375*i*	576*i*	494*i*	426*i*	365*i*	572*i*	486*i*	419*i*	357*i*
ω_2 [cm^{-1}]	130	89	80	71	129	95	92	71	125	77	60	65
ω_3 [cm^{-1}]	235	180	163	146	230	178	160	143	231	179	161	143
ω_4 [cm^{-1}]	264	197	176	155	260	194	172	151	260	196	174	151
ω_5 [cm^{-1}]	288	222	184	169	282	217	180	162	282	217	179	162
ω_6 [cm^{-1}]	534	427	403	377	533	432	401	373	531	426	395	370
ω_7 [cm^{-1}]	1007	944	912	872	988	925	896	854	982	922	890	854
ω_8 [cm^{-1}]	1042	968	933	891	1026	950	916	872	1021	946	911	870
ω_9 [cm^{-1}]	1113	1035	997	960	1100	1019	991	963	1094	1018	993	969
ω_{10} [cm^{-1}]	1393	1400	1401	1401	1399	1407	1412	1413	1400	1409	1411	1415
ω_{11} [cm^{-1}]	1397	1403	1402	1402	1401	1408	1413	1414	1401	1411	1414	1417
ω_{12} [cm^{-1}]	2725	2718	2717	2715	2681	2675	2673	2671	2680	2673	2671	2669
ω_{13} [cm^{-1}]	3192	3205	3198	3189	3173	3187	3182	3173	3175	3187	3181	3173
ω_{14} [cm^{-1}]	3397	3408	3399	3385	3359	3374	3366	3354	3361	3374	3366	3353
ω_{15} [cm^{-1}]	3416	3422	3412	3397	3376	3385	3376	3363	3376	3385	3376	3361

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

Table S4. Energies, structures, and frequencies for the DITS [Y = F, Cl, Br, I] double-inversion transition states (C_s symmetry) obtained at different levels of theory

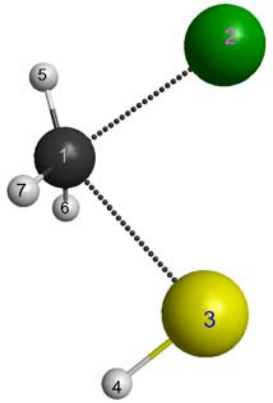


1	H						
2	S	1	r_1				
3	H	2	r_2	1	a_1		
4	C	3	r_3	2	a_2	1	180.0
5	Y	4	r_4	3	a_3	2	0.0
6	H	4	r_5	5	a_4	2	d_1
7	H	4	r_5	5	a_4	2	$-d_1$

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	$[FCH_2\cdots HSH]^-$	$[ClCH_2\cdots HSH]^-$	$[BrCH_2\cdots HSH]^-$	$[ICH_2\cdots HSH]^-$	$[FCH_2\cdots HSH]^-$	$[ClCH_2\cdots HSH]^-$	$[BrCH_2\cdots HSH]^-$	$[ICH_2\cdots HSH]^-$	$[FCH_2\cdots HSH]^-$	$[ClCH_2\cdots HSH]^-$	$[BrCH_2\cdots HSH]^-$	$[ICH_2\cdots HSH]^-$
Energy [E_h]	−537.622646	−897.649146	−853.617084	−732.767706	−537.864861	−897.862521	−853.826087	−732.972482	−537.909766	−897.917112	−853.883278	−733.020858
r_1 [Å]	1.351	1.351	1.351	1.351	1.341	1.341	1.341	1.341	1.340	1.340	1.340	1.340
r_2 [Å]	1.532	1.494	1.495	1.486	1.524	1.473	1.476	1.459	1.523	1.475	1.478	1.460
r_3 [Å]	1.731	1.795	1.796	1.823	1.732	1.822	1.816	1.864	1.733	1.815	1.810	1.861
r_4 [Å]	1.456	1.813	1.951	2.131	1.426	1.780	1.933	2.104	1.427	1.787	1.935	2.105
r_5 [Å]	1.095	1.091	1.091	1.091	1.083	1.080	1.079	1.079	1.082	1.078	1.077	1.077
a_1 [deg]	88.3	89.3	89.8	90.5	88.8	90.0	90.4	91.0	88.9	90.1	90.4	91.0
a_2 [deg]	195.4	187.7	184.4	180.2	196.8	188.8	185.3	181.9	196.4	188.5	185.2	182.1
a_3 [deg]	87.8	89.8	90.4	91.6	88.1	89.8	90.8	92.2	88.2	89.8	90.7	92.1
a_4 [deg]	110.4	111.7	112.0	112.8	111.9	113.6	113.6	114.5	111.8	113.4	113.4	114.4
d_1 [deg]	68.0	69.8	70.7	71.7	71.1	73.6	75.1	76.4	70.9	73.6	74.9	76.4
ZPE [cm^{-1}]	8668	8520	8405	8323	8627	8444	8374	8314	8619	8483	8364	8293
ω_1 [cm^{-1}]	924i	820i	843i	822i	1021i	838i	892i	837i	1013i	851i	901i	844i
ω_2 [cm^{-1}]	105	100	84	76	106	95	75	66	101	97	80	73
ω_3 [cm^{-1}]	147	151	145	137	147	124	147	153	136	155	149	136
ω_4 [cm^{-1}]	373	322	310	287	349	287	270	243	351	290	278	247
ω_5 [cm^{-1}]	398	382	381	373	387	359	364	346	392	369	368	347
ω_6 [cm^{-1}]	437	420	411	407	444	377	420	411	444	421	420	410
ω_7 [cm^{-1}]	854	713	624	578	864	713	616	573	861	711	612	570
ω_8 [cm^{-1}]	917	834	832	812	947	813	835	800	942	828	836	799
ω_9 [cm^{-1}]	1095	1016	965	913	1066	1010	949	887	1062	1003	946	884
ω_{10} [cm^{-1}]	1134	1151	1141	1151	1136	1183	1180	1199	1140	1179	1173	1196
ω_{11} [cm^{-1}]	1289	1344	1321	1309	1290	1369	1331	1309	1290	1360	1323	1302
ω_{12} [cm^{-1}]	1412	1377	1353	1362	1416	1399	1364	1450	1419	1386	1350	1434
ω_{13} [cm^{-1}]	2749	2748	2747	2748	2716	2716	2716	2717	2714	2715	2713	2713
ω_{14} [cm^{-1}]	3140	3167	3170	3170	3121	3150	3162	3160	3123	3153	3162	3160
ω_{15} [cm^{-1}]	3286	3315	3325	3325	3264	3292	3318	3315	3263	3297	3318	3315

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

Table S5. Energies, structures, and frequencies for the FSTS [Y = Cl, Br, I] front-side attack transition states (C_s symmetry) obtained at different levels of theory

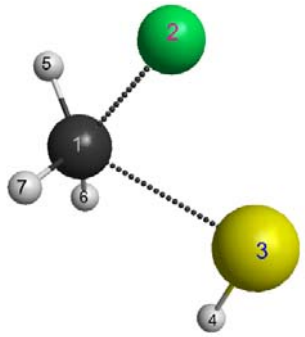


1	C						
2	Y	1	r_1				
3	S	1	r_2	2	a_1		
4	H	3	r_3	1	a_2	2	180.0
5	H	1	r_4	2	a_3	3	180.0
6	H	1	r_5	3	a_4	2	d_1
7	H	1	r_5	3	a_4	2	$-d_1$

Level[a]	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
System	$[Cl\cdots CH_3\cdots SH]^-$	$[Br\cdots CH_3\cdots SH]^-$	$[I\cdots CH_3\cdots SH]^-$	$[Cl\cdots CH_3\cdots SH]^-$	$[Br\cdots CH_3\cdots SH]^-$	$[I\cdots CH_3\cdots SH]^-$	$[Cl\cdots CH_3\cdots SH]^-$	$[Br\cdots CH_3\cdots SH]^-$	$[I\cdots CH_3\cdots SH]^-$
Energy [E_h]	−897.654104	−853.625586	−732.776909	−897.866917	−853.836619	−732.983330	−897.922553	−853.894836	−733.032573
r_1 [Å]	2.353	2.495	2.704	2.396	2.549	2.768	2.399	2.549	2.768
r_2 [Å]	2.527	2.551	2.582	2.582	2.624	2.667	2.583	2.621	2.664
r_3 [Å]	1.359	1.359	1.359	1.351	1.351	1.351	1.349	1.349	1.349
r_4 [Å]	1.093	1.093	1.092	1.079	1.079	1.079	1.078	1.078	1.077
r_5 [Å]	1.092	1.092	1.093	1.081	1.080	1.080	1.079	1.079	1.079
a_1 [deg]	81.8	82.7	83.6	81.3	82.7	83.6	81.6	82.5	83.3
a_2 [deg]	86.2	86.1	87.5	86.3	85.5	87.1	86.5	86.3	88.3
a_3 [deg]	73.4	73.2	73.1	72.0	71.4	71.0	71.6	71.2	70.9
a_4 [deg]	79.6	79.3	79.0	77.4	76.4	75.7	77.3	76.5	75.9
d_1 [deg]	121.1	121.0	120.9	119.9	119.3	118.8	119.9	119.4	118.9
ZPE [cm^{-1}]	9597	9526	9435	9437	9326	9298	9434	9357	9173
ω_1 [cm^{-1}]	626*i*	578*i*	549*i*	620*i*	568*i*	553*i*	610*i*	568*i*	555*i*
ω_2 [cm^{-1}]	66	91	96	93	69	91	56	83	45*i*
ω_3 [cm^{-1}]	161	131	112	137	107	143	135	108	86
ω_4 [cm^{-1}]	220	207	192	211	182	197	204	192	156
ω_5 [cm^{-1}]	346	327	297	308	282	257	306	284	238
ω_6 [cm^{-1}]	510	486	445	460	432	400	463	433	385
ω_7 [cm^{-1}]	736	718	695	685	658	640	688	663	625
ω_8 [cm^{-1}]	831	793	758	761	724	683	776	729	672
ω_9 [cm^{-1}]	1120	1095	1071	1056	1031	997	1072	1040	1008
ω_{10} [cm^{-1}]	1433	1431	1430	1439	1434	1434	1442	1439	1433
ω_{11} [cm^{-1}]	1478	1476	1473	1470	1461	1460	1470	1465	1457
ω_{12} [cm^{-1}]	2678	2680	2679	2625	2630	2631	2624	2627	2626
ω_{13} [cm^{-1}]	3115	3116	3118	3118	3121	3128	3120	3123	3125
ω_{14} [cm^{-1}]	3227	3229	3233	3243	3251	3262	3246	3254	3260
ω_{15} [cm^{-1}]	3274	3273	3270	3265	3271	3275	3267	3273	3276

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

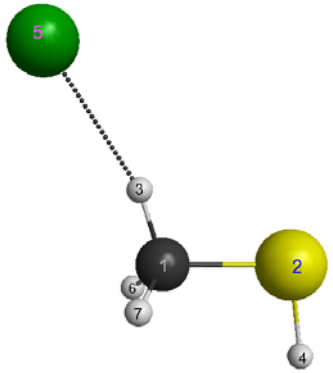
Table S6. Energies, structures, and frequencies for the FSTS [Y = F] front-side attack transition states (C_1 symmetry) obtained at different levels of theory



1	C						
2	Y	1	r_1				
3	S	1	r_2	2	a_1		
4	H	3	r_3	1	a_2	2	d_1
5	H	1	r_4	2	a_3	3	d_2
6	H	1	r_5	3	a_4	2	d_3
7	H	1	r_6	3	a_5	2	d_4

Level	MP2/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVTZ
Energy [E_h]	−537.629571	−537.867769	−537.913675
r_1 [Å]	1.817	1.829	1.833
r_2 [Å]	2.377	2.392	2.398
r_3 [Å]	1.360	1.352	1.351
r_4 [Å]	1.103	1.090	1.088
r_5 [Å]	1.103	1.091	1.088
r_6 [Å]	1.094	1.082	1.080
a_1 [deg]	76.8	76.4	76.4
a_2 [deg]	91.6	92.3	92.6
a_3 [deg]	79.9	79.1	79.0
a_4 [deg]	77.9	76.8	76.4
a_5 [deg]	99.5	98.9	99.2
d_1 [deg]	181.8	182.6	183.2
d_2 [deg]	209.8	210.4	211.0
d_3 [deg]	155.9	156.0	156.6
d_4 [deg]	−94.8	−93.9	−93.3
ZPE [cm^{-1}]	9906	9841	9820
ω_1 [cm^{-1}]	659i	694i	690i
ω_2 [cm^{-1}]	186	194	168
ω_3 [cm^{-1}]	251	236	232
ω_4 [cm^{-1}]	267	278	261
ω_5 [cm^{-1}]	457	421	417
ω_6 [cm^{-1}]	619	607	604
ω_7 [cm^{-1}]	873	864	860
ω_8 [cm^{-1}]	1006	985	979
ω_9 [cm^{-1}]	1230	1218	1220
ω_{10} [cm^{-1}]	1414	1427	1430
ω_{11} [cm^{-1}]	1520	1517	1517
ω_{12} [cm^{-1}]	2666	2611	2609
ω_{13} [cm^{-1}]	3027	3031	3037
ω_{14} [cm^{-1}]	3069	3077	3088
ω_{15} [cm^{-1}]	3228	3214	3218

Table S7. Energies, structures, and frequencies for the PostHMIN2 [Y = F, Cl, Br, I] H-bonded complexes (C_s symmetry) obtained at different levels of theory

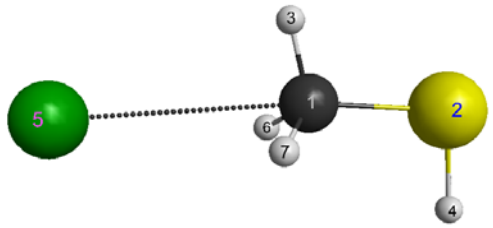


1	C							
2	S	1	r_1					
3	H	1	r_2	2	a_1			
4	H	2	r_3	1	a_2	3	180.0	
5	Y	3	r_4	2	a_3	1	0.0	
6	H	1	r_5	2	a_4	3	d_1	
7	H	1	r_5	2	a_4	3	$-d_1$	

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ		
System	**F^-···HCH_2SH**	**Cl^-···HCH_2SH**	**Br^-···HCH_2SH**	**I^-···HCH_2SH**	**F^-···HCH_2SH**	**Cl^-···HCH_2SH**	**Br^-···HCH_2SH**	**I^-···HCH_2SH**	**F^-···HCH_2SH**	**Cl^-···HCH_2SH**	**Br^-···HCH_2SH**
Energy [E_h]	−537.722143	−897.768427	−853.740682	−732.893725	−537.960883	−897.979258	−853.950737	−733.099381	−538.005872	−898.034205	−854.007816
r_1 [Å]	1.838	1.837	1.836	1.838	1.817	1.817	1.817	1.819	1.817	1.817	1.818
r_2 [Å]	1.140	1.106	1.104	1.099	1.132	1.098	1.096	1.091	1.131	1.096	1.093
r_3 [Å]	1.354	1.352	1.352	1.351	1.345	1.343	1.343	1.342	1.344	1.341	1.341
r_4 [Å]	1.647	2.429	2.616	2.999	1.633	2.425	2.624	3.006	1.632	2.420	2.653
r_5 [Å]	1.101	1.099	1.098	1.097	1.092	1.090	1.089	1.088	1.090	1.088	1.087
a_1 [deg]	107.5	107.7	107.8	108.1	107.5	108.0	107.8	108.1	107.4	107.9	108.1
a_2 [deg]	98.9	97.6	97.4	97.3	99.1	97.7	97.6	97.5	99.2	97.9	97.7
a_3 [deg]	221.4	210.7	207.1	182.6	221.6	209.3	207.1	182.5	221.5	208.2	199.3
a_4 [deg]	109.5	110.2	110.4	110.8	109.8	110.5	110.6	111.0	109.7	110.4	110.5
d_1 [deg]	119.6	118.8	118.7	118.3	119.5	118.7	118.6	118.3	119.5	118.7	118.6
ZPE [cm^{-1}]	10202	10282	10261	10200	10156	10227	10219	10161	10166	10240	10220
ω_1 [cm^{-1}]	85	43	34	30*i*	84	39	25	17*i*	83	42	33
ω_2 [cm^{-1}]	212	139	110	67	218	132	107	66	211	132	98
ω_3 [cm^{-1}]	263	145	131	82	268	141	134	81	268	135	116
ω_4 [cm^{-1}]	380	287	276	249	382	285	276	250	381	283	270
ω_5 [cm^{-1}]	695	705	706	702	701	710	712	709	700	709	709
ω_6 [cm^{-1}]	812	799	796	781	819	803	805	788	818	803	798
ω_7 [cm^{-1}]	1007	989	986	977	1008	990	987	977	1012	993	990
ω_8 [cm^{-1}]	1074	1078	1077	1065	1086	1088	1091	1079	1088	1091	1086
ω_9 [cm^{-1}]	1401	1364	1359	1339	1418	1381	1377	1360	1422	1383	1374
ω_{10} [cm^{-1}]	1472	1463	1463	1460	1484	1478	1479	1477	1490	1485	1485
ω_{11} [cm^{-1}]	1509	1477	1471	1460	1523	1493	1489	1478	1530	1498	1492
ω_{12} [cm^{-1}]	2542	2728	2731	2738	2501	2688	2692	2699	2499	2688	2692
ω_{13} [cm^{-1}]	2706	3018	3040	3084	2663	2987	3011	3055	2663	2988	3024
ω_{14} [cm^{-1}]	3090	3144	3154	3191	3052	3101	3111	3146	3057	3105	3121
ω_{15} [cm^{-1}]	3154	3185	3188	3204	3106	3137	3142	3158	3112	3144	3151

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

Table S8. Energies, structures, and frequencies for the WaldenPostMIN [Y = Cl, Br, I] ion-dipole complexes (C_s symmetry) obtained at different levels of theory

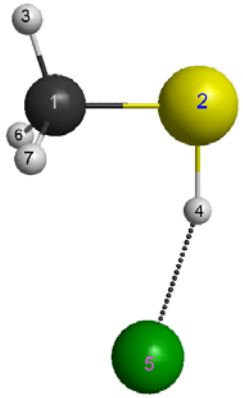


1	C							
2	S	1	r_1					
3	H	1	r_2	2	a_1			
4	H	2	r_3	1	a_2	3	180.0	
5	Y	1	r_4	3	a_3	2	180.0	
6	H	1	r_5	2	a_4	3	d_1	
7	H	1	r_5	2	a_4	3	$-d_1$	

Level[a]	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
System	**Cl^-···CH_3SH**	**Br^-···CH_3SH**	**I^-···CH_3SH**	**Cl^-···CH_3SH**	**Br^-···CH_3SH**	**I^-···CH_3SH**	**Cl^-···CH_3SH**	**Br^-···CH_3SH**	**I^-···CH_3SH**
Energy [E_h]	−897.768230	−853.740951	−732.894436	−897.979014	−853.950986	−733.099989	−898.033951	−854.008086	−733.148193
r_1 [Å]	1.846	1.845	1.843	1.825	1.825	1.824	1.826	1.825	1.824
r_2 [Å]	1.097	1.098	1.098	1.089	1.089	1.089	1.087	1.087	1.088
r_3 [Å]	1.350	1.350	1.350	1.341	1.341	1.341	1.339	1.339	1.339
r_4 [Å]	3.291	3.465	3.706	3.282	3.468	3.712	3.287	3.474	3.735
r_5 [Å]	1.095	1.095	1.095	1.086	1.086	1.087	1.084	1.085	1.085
a_1 [deg]	106.7	106.6	106.6	106.8	106.9	106.9	106.7	106.7	106.7
a_2 [deg]	97.0	97.0	96.9	97.3	97.2	97.1	97.4	97.3	97.2
a_3 [deg]	80.0	81.6	80.6	80.8	81.3	80.4	81.5	81.5	80.6
a_4 [deg]	111.8	111.8	111.7	112.2	112.0	111.9	112.0	111.9	111.7
d_1 [deg]	118.4	118.4	118.4	118.4	118.5	118.4	118.5	118.5	118.5
ZPE [cm^{-1}]	10196	10194	10197	10139	10151	10148	10155	10158	10160
ω_1 [cm^{-1}]	33	33	32	28	31	27	19	25	25
ω_2 [cm^{-1}]	41	44	46	30	63	43	27	38	40
ω_3 [cm^{-1}]	99	76	64	98	80	62	96	72	60
ω_4 [cm^{-1}]	221	225	227	221	217	227	227	231	228
ω_5 [cm^{-1}]	683	687	692	692	695	698	689	693	697
ω_6 [cm^{-1}]	771	774	778	776	777	782	775	779	782
ω_7 [cm^{-1}]	937	942	948	929	939	948	938	945	953
ω_8 [cm^{-1}]	1066	1070	1072	1079	1080	1084	1080	1083	1085
ω_9 [cm^{-1}]	1311	1317	1322	1331	1337	1343	1334	1340	1346
ω_{10} [cm^{-1}]	1446	1448	1450	1462	1464	1466	1470	1472	1473
ω_{11} [cm^{-1}]	1454	1456	1459	1473	1471	1477	1481	1483	1485
ω_{12} [cm^{-1}]	2749	2747	2747	2707	2707	2708	2707	2705	2708
ω_{13} [cm^{-1}]	3117	3113	3109	3085	3082	3079	3089	3084	3080
ω_{14} [cm^{-1}]	3223	3219	3216	3174	3170	3168	3180	3174	3171
ω_{15} [cm^{-1}]	3241	3236	3232	3192	3187	3184	3198	3191	3186

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

Table S9. Energies, structures, and frequencies for the PostHMIN [Y = F, Cl, Br, I] H-bonded complexes (C_s symmetry) obtained at different levels of theory

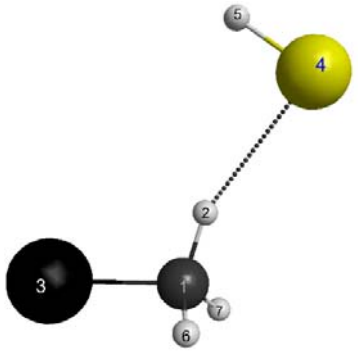


1	C						
2	S	1	r_1				
3	H	1	r_2	2	a_1		
4	H	2	r_3	1	a_2	3	180.0
5	Y	4	r_4	2	a_3	1	0.0
6	H	1	r_5	2	a_4	3	d_1
7	H	1	r_5	2	a_4	3	$-d_1$

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	$CH_3SH\cdots F^-$	$CH_3SH\cdots Cl^-$	$CH_3SH\cdots Br^-$	$CH_3SH\cdots I^-$	$CH_3SH\cdots F^-$	$CH_3SH\cdots Cl^-$	$CH_3SH\cdots Br^-$	$CH_3SH\cdots I^-$	$CH_3SH\cdots F^-$	$CH_3SH\cdots Cl^-$	$CH_3SH\cdots Br^-$	$CH_3SH\cdots I^-$
Energy [E_h]	−537.757849	−897.776606	−853.747862	−732.899868	−537.997367	−897.986686	−853.957132	−733.104772	−538.042758	−898.041573	−854.014193	−733.152857
r_1 [Å]	1.844	1.833	1.832	1.832	1.828	1.814	1.814	1.814	1.829	1.815	1.815	1.814
r_2 [Å]	1.105	1.101	1.101	1.101	1.096	1.093	1.092	1.092	1.094	1.091	1.090	1.090
r_3 [Å]	1.925	1.391	1.378	1.370	1.947	1.375	1.365	1.358	1.951	1.375	1.363	1.356
r_4 [Å]	1.003	2.123	2.360	2.668	0.986	2.158	2.409	2.715	0.985	2.157	2.409	2.731
r_5 [Å]	1.104	1.099	1.098	1.098	1.096	1.090	1.089	1.089	1.094	1.088	1.088	1.088
a_1 [deg]	110.7	108.4	108.1	107.7	110.8	108.4	108.0	107.7	110.6	108.3	108.0	107.5
a_2 [deg]	93.9	92.3	92.6	93.2	95.0	92.8	93.3	93.9	95.8	92.9	93.4	94.1
a_3 [deg]	176.7	161.1	157.5	154.1	177.0	158.8	154.7	151.9	177.6	159.1	154.6	151.8
a_4 [deg]	111.4	110.0	110.0	110.1	111.4	110.1	110.1	110.2	111.4	110.0	110.0	110.2
d_1 [deg]	119.9	120.1	120.1	120.0	119.9	120.2	120.1	120.0	119.9	120.1	120.1	120.0
ZPE [cm^{-1}]	10423	10186	10218	10239	10492	10179	10211	10218	10492	10189	10198	10219
ω_1 [cm^{-1}]	46	10*i*	10	29	58	42*i*	22	46	31*i*	56*i*	41*i*	32
ω_2 [cm^{-1}]	78	76	72	72	72	79	80	73	74	73	74	72
ω_3 [cm^{-1}]	257	149	119	100	258	150	116	99	257	152	114	95
ω_4 [cm^{-1}]	719	565	507	451	723	549	482	428	721	546	478	421
ω_5 [cm^{-1}]	904	730	729	726	873	735	732	731	893	733	731	730
ω_6 [cm^{-1}]	933	863	849	836	929	855	846	833	930	855	840	831
ω_7 [cm^{-1}]	943	972	974	976	944	976	980	978	945	979	982	983
ω_8 [cm^{-1}]	1041	1102	1095	1091	1024	1113	1108	1105	1024	1113	1106	1105
ω_9 [cm^{-1}]	1308	1328	1331	1334	1327	1350	1352	1355	1327	1351	1354	1357
ω_{10} [cm^{-1}]	1462	1449	1449	1449	1477	1461	1463	1462	1483	1468	1468	1468
ω_{11} [cm^{-1}]	1465	1469	1468	1467	1481	1486	1485	1484	1488	1492	1491	1491
ω_{12} [cm^{-1}]	2486	2254	2405	2509	2751	2315	2443	2523	2761	2306	2438	2524
ω_{13} [cm^{-1}]	3016	3067	3070	3072	2984	3036	3042	3043	2987	3042	3045	3046
ω_{14} [cm^{-1}]	3093	3169	3174	3177	3041	3122	3130	3132	3046	3129	3133	3135
ω_{15} [cm^{-1}]	3095	3178	3184	3188	3043	3132	3141	3145	3048	3139	3145	3148

[a] For Br and I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.

Table S10. Energies, structures, and frequencies for the HMIN [Y = I] H-bonded complexes (C_s symmetry) obtained at different levels of theory



1	C						
2	H	1	r_1				
3	Y	1	r_2	2	a_1		
4	S	2	r_3	1	a_2	3	180.0
5	H	4	r_4	2	a_3	1	180.0
6	H	1	r_5	3	a_4	2	d_1
7	H	1	r_5	3	a_4	2	$-d_1$

Level[a]	MP2/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVTZ
Energy [E_h]	−732.844151	−733.047401	−733.096079
r_1 [Å]	1.108	1.097	1.095
r_2 [Å]	2.172	2.157	2.159
r_3 [Å]	2.462	2.487	2.506
r_4 [Å]	1.356	1.347	1.345
r_5 [Å]	1.097	1.087	1.085
a_1 [deg]	109.2	109.3	109.4
a_2 [deg]	162.4	159.8	155.5
a_3 [deg]	88.1	88.8	90.4
a_4 [deg]	106.3	106.3	106.2
d_1 [deg]	120.7	120.6	120.5
ZPE [cm^{-1}]	9564	9507	9497
ω_1 [cm^{-1}]	18	34*i*	37*i*
ω_2 [cm^{-1}]	31	35	31
ω_3 [cm^{-1}]	122	128	124
ω_4 [cm^{-1}]	144	138	131
ω_5 [cm^{-1}]	185	161	146
ω_6 [cm^{-1}]	529	523	519
ω_7 [cm^{-1}]	913	909	902
ω_8 [cm^{-1}]	918	916	914
ω_9 [cm^{-1}]	1300	1305	1301
ω_{10} [cm^{-1}]	1442	1459	1462
ω_{11} [cm^{-1}]	1459	1478	1481
ω_{12} [cm^{-1}]	2703	2660	2658
ω_{13} [cm^{-1}]	2976	2973	2986
ω_{14} [cm^{-1}]	3166	3140	3147
ω_{15} [cm^{-1}]	3221	3189	3195

[a] For I effective core potentials and the corresponding aug-cc-pVDZ-PP and aug-cc-pVTZ-PP basis sets are employed.