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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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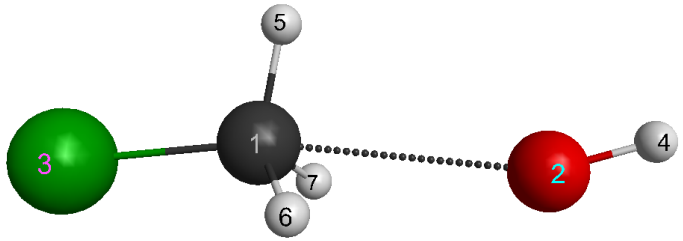
Content

Energies, structures, and frequencies for the stationary points of the potential energy surface of the $OH^- + CH_3Y$ [Y = F, Cl, Br, I] S_N2 reactions obtained at different levels of theory (data are taken from D. A. Tasi, Z. Fábián and G. Czakó, *J. Phys. Chem. A*, 2018, **122**, 5773)

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

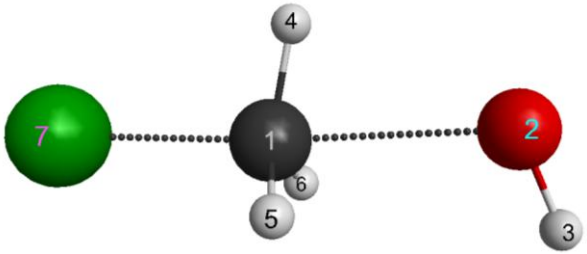


1	C						
2	O	1	r_1				
3	Y	1	r_2	2	a_1		
4	H	2	r_3	1	a_2	3	180.0
5	H	1	r_4	3	a_3	2	180.0
6	H	1	r_5	3	a_4	5	d_1
7	H	1	r_5	3	a_4	5	$-d_1$

Level[a]	**MP2/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVTZ**		
System	**$FCH_3\cdots OH^-$**	**$ClCH_3\cdots OH^-$**	**$BrCH_3\cdots OH^-$**	**$FCH_3\cdots OH^-$**	**$ClCH_3\cdots OH^-$**	**$BrCH_3\cdots OH^-$**	**$FCH_3\cdots OH^-$**	**$ClCH_3\cdots OH^-$**	**$BrCH_3\cdots OH^-$**
Energy [E_h]	−215.076647	−−575.087560	−531.052094	−215.329005	−575.310262	−531.271684	−215.366077	−575.357305	−531.321117
r_1 [Å]	2.664	2.614	2.578	2.656	2.611	2.545	2.649	2.600	2.532
r_2 [Å]	1.453	1.849	2.011	1.423	1.826	2.016	1.424	1.834	2.022
r_3 [Å]	0.971	0.971	0.971	0.963	0.963	0.963	0.963	0.963	0.963
r_4 [Å]	1.094	1.092	1.091	1.086	1.083	1.080	1.085	1.081	1.079
r_5 [Å]	1.092	1.091	1.090	1.085	1.082	1.080	1.083	1.080	1.078
a_1 [deg]	171.9	169.1	168.9	170.1	168.2	170.3	170.6	168.6	170.3
a_2 [deg]	161.8	158.7	148.6	156.6	154.5	134.8	158.2	154.6	134.9
a_3 [deg]	107.7	107.1	106.1	108.3	107.6	105.9	108.3	107.3	105.6
a_4 [deg]	108.6	108.3	107.6	109.4	109.0	107.2	109.3	108.7	106.9
d_1 [deg]	120.1	120.2	120.1	120.1	120.2	120.0	120.1	120.2	120.0
ZPE [cm^{-1}]	10791	10450	10290	10711	10387	10242	10753	10413	10231
ω_1 [cm^{-1}]	44*i*	24	38	97*i*	30*i*	59	56*i*	20	58
ω_2 [cm^{-1}]	93	82	86	85	80	94	94	84	74
ω_3 [cm^{-1}]	165	159	137	124	158	111	157	150	113
ω_4 [cm^{-1}]	174	175	165	158	162	174	169	176	170
ω_5 [cm^{-1}]	188	192	185	184	188	196	188	190	196
ω_6 [cm^{-1}]	904	622	502	948	615	457	941	617	450
ω_7 [cm^{-1}]	1114	960	898	1119	959	892	1122	953	888
ω_8 [cm^{-1}]	1131	990	928	1145	997	920	1146	987	917
ω_9 [cm^{-1}]	1392	1283	1226	1404	1295	1211	1409	1298	1211
ω_{10} [cm^{-1}]	1470	1439	1428	1479	1459	1444	1485	1465	1447
ω_{11} [cm^{-1}]	1470	1442	1430	1483	1459	1447	1489	1467	1452
ω_{12} [cm^{-1}]	3144	3157	3161	3096	3127	3144	3101	3132	3146
ω_{13} [cm^{-1}]	3270	3292	3304	3199	3240	3273	3204	3248	3277
ω_{14} [cm^{-1}]	3280	3298	3309	3215	3248	3282	3218	3256	3286
ω_{15} [cm^{-1}]	3788	3785	3783	3783	3785	3781	3783	3783	3778

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

Table S2. Energies, structures, and frequencies for the WaldenTS [Y = F, Cl, Br] transition states (C_s symmetry) obtained at different levels of theory

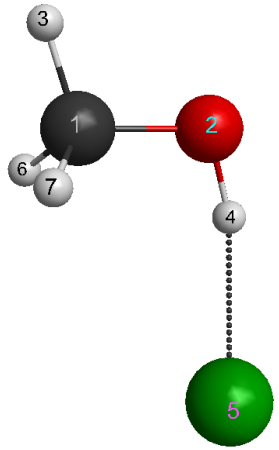


1	C							
2	O	1	r_1					
3	H	2	r_2	1	a_1			
4	H	1	r_3	2	a_2	3	180.0	
5	H	1	r_4	4	a_3	2	d_1	
6	H	1	r_4	4	a_3	2	$-d_1$	
7	Y	1	r_5	4	a_4	2	180.0	

Level[a]	**MP2/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVTZ**		
System	**$[F{\cdot}CH_3{\cdot}OH]^-$**	**$[Cl{\cdot}CH_3{\cdot}OH]^-$**	**$[Br{\cdot}CH_3{\cdot}OH]^-$**	**$[F{\cdot}CH_3{\cdot}OH]^-$**	**$[Cl{\cdot}CH_3{\cdot}OH]^-$**	**$[Br{\cdot}CH_3{\cdot}OH]^-$**	**$[F{\cdot}CH_3{\cdot}OH]^-$**	**$[Cl{\cdot}CH_3{\cdot}OH]^-$**	**$[Br{\cdot}CH_3{\cdot}OH]^-$**
Energy [E_h]	−215.061411	−575.083708	−531.051006	−215.310794	−575.306035	−531.271222	−215.348288	−575.353404	−531.320799
r_1 [Å]	2.010	2.237	2.325	1.988	2.223	2.345	1.991	2.227	2.364
r_2 [Å]	0.971	0.972	0.972	0.963	0.964	0.964	0.963	0.964	0.964
r_3 [Å]	1.083	1.084	1.086	1.073	1.074	1.076	1.072	1.072	1.075
r_4 [Å]	1.083	1.083	1.085	1.074	1.074	1.076	1.072	1.072	1.074
r_5 [Å]	1.755	2.056	2.147	1.754	2.057	2.129	1.754	2.053	2.117
a_1 [deg]	106.0	110.0	112.6	105.0	107.5	110.7	104.8	107.8	112.4
a_2 [deg]	83.3	76.6	73.8	84.2	77.5	73.8	84.2	77.1	72.9
a_3 [deg]	119.3	117.1	115.8	119.4	117.1	115.3	119.3	117.0	115.0
a_4 [deg]	93.9	99.7	101.9	93.6	99.7	102.6	93.7	99.8	103.1
d_1 [deg]	84.2	74.4	71.1	84.8	74.5	70.0	84.7	74.3	69.3
ZPE [cm^{-1}]	10916	10501	10303	10850	10423	10216	10825	10415	10176
ω_1 [cm^{-1}]	565*i*	424*i*	299*i*	602*i*	434*i*	254*i*	600*i*	426*i*	216*i*
ω_2 [cm^{-1}]	167	114	88	168	103	67	143	83	36
ω_3 [cm^{-1}]	305	205	169	305	206	161	304	203	157
ω_4 [cm^{-1}]	328	219	181	328	217	172	328	217	166
ω_5 [cm^{-1}]	373	291	252	367	287	248	365	287	249
ω_6 [cm^{-1}]	672	481	414	683	490	399	674	477	376
ω_7 [cm^{-1}]	1098	980	924	1088	958	905	1083	960	905
ω_8 [cm^{-1}]	1122	990	931	1113	967	911	1109	971	910
ω_9 [cm^{-1}]	1231	1139	1112	1221	1122	1117	1214	1127	1127
ω_{10} [cm^{-1}]	1401	1406	1406	1401	1413	1422	1399	1417	1428
ω_{11} [cm^{-1}]	1402	1410	1410	1402	1416	1425	1400	1421	1432
ω_{12} [cm^{-1}]	3178	3200	3191	3154	3180	3169	3155	3180	3170
ω_{13} [cm^{-1}]	3386	3391	3372	3340	3354	3330	3343	3354	3328
ω_{14} [cm^{-1}]	3386	3397	3377	3342	3358	3333	3346	3357	3331
ω_{15} [cm^{-1}]	3784	3780	3779	3788	3776	3772	3787	3774	3771

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

Table S3. Energies, structures, and frequencies for the PostHMIN [Y = F, Cl, Br, I] H-bonded complexes (C_s symmetry) obtained at different levels of theory

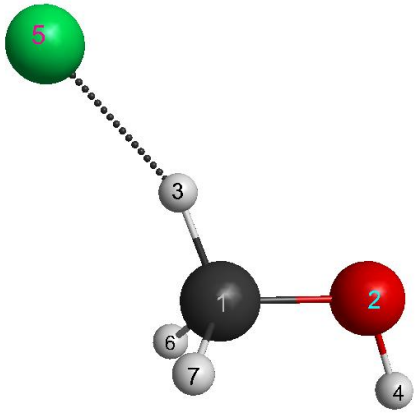


1	C						
2	O	1	r_1				
3	H	1	r_2	2	a_1		
4	H	2	r_3	1	a_2	3	180.0
5	Y	4	r_4	2	a_3	1	0.0
6	H	1	r_5	2	a_4	3	d_1
7	H	1	r_5	2	a_4	3	$-d_1$

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	**$CH_3OH\cdots F^-$**	**$CH_3OH\cdots Cl^-$**	**$CH_3OH\cdots Br^-$**	**$CH_3OH\cdots I^-$**	**$CH_3OH\cdots F^-$**	**$CH_3OH\cdots Cl^-$**	**$CH_3OH\cdots Br^-$**	**$CH_3OH\cdots I^-$**	**$CH_3OH\cdots F^-$**	**$CH_3OH\cdots Cl^-$**	**$CH_3OH\cdots Br^-$**	**$CH_3OH\cdots I^-$**
Energy [E_h]	−215.134521	−575.170641	−531.141221	−410.292504	−215.387088	−575.395174	−531.364831	−410.511585	−215.423961	−575.442094	−531.413905	−410.551631
r_1 [Å]	1.404	1.420	1.422	1.425	1.387	1.404	1.407	1.409	1.388	1.405	1.408	1.410
r_2 [Å]	1.108	1.103	1.103	1.102	1.101	1.096	1.095	1.094	1.099	1.094	1.093	1.092
r_3 [Å]	1.065	0.994	0.988	0.983	1.062	0.985	0.980	0.975	1.061	0.985	0.980	0.975
r_4 [Å]	1.372	2.104	2.307	2.578	1.344	2.101	2.304	2.578	1.345	2.097	2.303	2.584
r_5 [Å]	1.112	1.106	1.105	1.105	1.105	1.098	1.097	1.097	1.103	1.096	1.096	1.095
a_1 [deg]	109.6	107.7	107.4	107.2	110.0	108.1	107.8	107.6	109.9	108.1	107.8	107.5
a_2 [deg]	105.7	104.9	105.1	105.4	106.3	105.5	105.7	106.0	106.3	105.4	105.6	106.0
a_3 [deg]	175.7	166.9	165.2	163.8	175.7	166.2	164.6	163.2	175.8	166.8	164.7	163.4
a_4 [deg]	112.7	112.0	111.9	111.9	112.8	112.1	112.0	111.9	112.8	112.0	112.0	111.9
d_1 [deg]	119.6	119.5	119.5	119.4	119.7	119.6	119.5	119.5	119.7	119.6	119.5	119.5
ZPE [cm^{-1}]	11202	11491	11486	11478	11120	11482	11462	11480	11153	11485	11497	11487
ω_1 [cm^{-1}]	83	77	81	80	49	53	33	79	58	30	72	78
ω_2 [cm^{-1}]	163	108	92	82	162	110	94	83	164	110	95	85
ω_3 [cm^{-1}]	406	206	174	151	406	217	177	156	407	217	180	155
ω_4 [cm^{-1}]	1110	787	718	650	1137	775	707	640	1131	783	712	639
ω_5 [cm^{-1}]	1143	1080	1075	1068	1154	1106	1100	1094	1156	1102	1096	1089
ω_6 [cm^{-1}]	1160	1118	1113	1106	1170	1130	1124	1120	1173	1133	1126	1120
ω_7 [cm^{-1}]	1192	1170	1171	1170	1205	1184	1184	1185	1214	1183	1184	1183
ω_8 [cm^{-1}]	1434	1447	1447	1434	1450	1466	1466	1451	1455	1470	1470	1451
ω_9 [cm^{-1}]	1471	1473	1456	1452	1481	1484	1468	1470	1486	1489	1472	1474
ω_{10} [cm^{-1}]	1492	1474	1475	1476	1505	1485	1485	1488	1510	1490	1491	1493
ω_{11} [cm^{-1}]	1620	1510	1506	1505	1635	1521	1518	1518	1639	1525	1523	1522
ω_{12} [cm^{-1}]	2123	3015	3023	3030	2070	2976	2986	2992	2080	2979	2988	2994
ω_{13} [cm^{-1}]	2961	3084	3094	3103	2914	3024	3036	3045	2919	3028	3040	3049
ω_{14} [cm^{-1}]	2999	3114	3123	3132	2928	3053	3064	3074	2936	3058	3068	3078
ω_{15} [cm^{-1}]	3043	3319	3427	3516	2973	3378	3480	3566	2979	3373	3476	3564

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

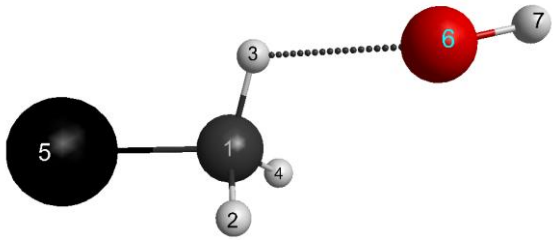
Table S4. Energies, structures, and frequencies for the [$F^-\cdots HCH_2OH$] H-bonded complexes (C_s symmetry) obtained at different levels of theory



1	C						
2	O	1	r_1				
3	H	1	r_2	2	a_1		
4	H	2	r_3	1	a_2	3	180.0
5	F	3	r_4	1	a_3	2	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	**MP2/aug-cc-pVDZ**	**CCSD(T)-F12b/aug-cc-pVDZ**	**CCSD(T)-F12b/aug-cc-pVTZ**
Energy [E_h]	−215.102006	−215.353465	−215.390333
r_1 [Å]	1.461	1.443	1.445
r_2 [Å]	1.114	1.107	1.105
r_3 [Å]	0.965	0.958	0.958
r_4 [Å]	1.833	1.814	1.817
r_5 [Å]	1.106	1.098	1.096
a_1 [deg]	110.5	111.0	111.1
a_2 [deg]	106.9	107.3	107.2
a_3 [deg]	160.3	159.8	159.2
a_4 [deg]	110.0	110.1	110.1
d_1 [deg]	120.2	120.2	120.2
ZPE [cm^{-1}]	11379	11375	11373
ω_1 [cm^{-1}]	100	106	100
ω_2 [cm^{-1}]	194	191	183
ω_3 [cm^{-1}]	201	212	210
ω_4 [cm^{-1}]	371	358	354
ω_5 [cm^{-1}]	962	990	985
ω_6 [cm^{-1}]	1055	1069	1067
ω_7 [cm^{-1}]	1178	1190	1190
ω_8 [cm^{-1}]	1320	1339	1339
ω_9 [cm^{-1}]	1476	1492	1496
ω_{10} [cm^{-1}]	1496	1512	1511
ω_{11} [cm^{-1}]	1530	1545	1547
ω_{12} [cm^{-1}]	2896	2861	2866
ω_{13} [cm^{-1}]	3060	3008	3013
ω_{14} [cm^{-1}]	3089	3026	3033
ω_{15} [cm^{-1}]	3833	3851	3852

Table S5. Energies, structures, and frequencies for the HTS [Y = Br, I] H-bonded transition states (C_1 symmetry) obtained at different levels of theory

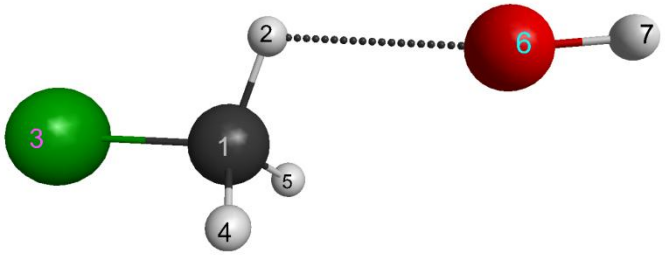


1	C						
2	H	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_3	2	a_2	3	d_1
5	Y	1	r_4	4	a_3	2	d_2
6	O	3	r_5	1	a_4	2	d_3
7	H	6	r_6	3	a_5	4	d_4

Level[a]	MP2/aug-cc-pVDZ		CCSD(T)-F12b/aug-cc-pVDZ		CCSD(T)-F12b/aug-cc-pVTZ	
System	$[OH\cdots HCH_2\cdots Br]^-$	$[OH\cdots HCH_2\cdots I]^-$	$[OH\cdots HCH_2\cdots Br]^-$	$[OH\cdots HCH_2\cdots I]^-$	$[OH\cdots HCH_2\cdots Br]^-$	$[OH\cdots HCH_2\cdots I]^-$
Energy [E_h]	−531.051907	−410.197092	−531.271324	−410.411903	−531.320719	−410.452219
r_1 [Å]	1.093	1.092	1.083	1.083	1.081	1.081
r_2 [Å]	1.094	1.094	1.085	1.085	1.084	1.084
r_3 [Å]	1.093	1.093	1.084	1.083	1.082	1.082
r_4 [Å]	1.993	2.203	1.986	2.196	1.988	2.196
r_5 [Å]	2.063	2.069	2.042	2.045	2.025	2.034
r_6 [Å]	0.971	0.972	0.963	0.963	0.963	0.963
a_1 [deg]	110.6	110.4	110.2	110.5	110.5	110.7
a_2 [deg]	111.9	112.3	111.9	112.2	112.0	112.4
a_3 [deg]	106.4	105.7	106.2	105.5	106.0	105.3
a_4 [deg]	111.3	108.6	112.3	110.2	113.7	110.9
a_5 [deg]	169.6	157.3	159.4	142.2	160.5	146.1
d_1 [deg]	124.4	125.4	124.2	125.3	124.7	125.8
d_2 [deg]	−116.1	−115.8	−116.1	−115.4	−115.7	−115.1
d_3 [deg]	59.1	51.9	53.5	51.52	54.8	52.45
d_4 [deg]	117.2	80.6	86.6	69.9	88.7	80.0
ZPE [cm^{-1}]	10276	10139	10225	10066	10258	10091
ω_1 [cm^{-1}]	72*i*	82*i*	97*i*	104*i*	78*i*	98*i*
ω_2 [cm^{-1}]	39	82	67	75	81	92
ω_3 [cm^{-1}]	167	143	124	144	135	139
ω_4 [cm^{-1}]	179	178	186	177	188	184
ω_5 [cm^{-1}]	205	194	190	183	201	185
ω_6 [cm^{-1}]	547	477	537	451	536	453
ω_7 [cm^{-1}]	886	812	876	783	883	792
ω_8 [cm^{-1}]	953	891	949	884	953	885
ω_9 [cm^{-1}]	1258	1202	1265	1195	1272	1202
ω_{10} [cm^{-1}]	1436	1424	1451	1439	1458	1444
ω_{11} [cm^{-1}]	1437	1427	1460	1453	1466	1456
ω_{12} [cm^{-1}]	3128	3127	3103	3102	3102	3102
ω_{13} [cm^{-1}]	3264	3265	3224	3226	3223	3226
ω_{14} [cm^{-1}]	3275	3280	3233	3241	3235	3243
ω_{15} [cm^{-1}]	3779	3778	3785	3781	3783	3780

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

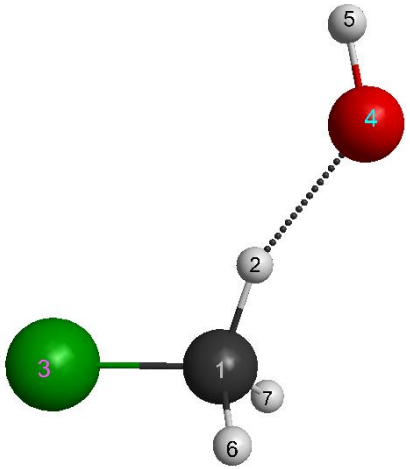
Table S6. Energies, structures, and frequencies for the HTS [Y = Cl] H-bonded transition states (C_s symmetry) obtained at different levels of theory



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

Level	MP2/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVDZ	CCSD(T)-F12b/aug-cc-pVTZ
Energy [E_h]	−575.087425	−575.310238	−575.357197
r_1 [Å]	1.094	1.084	1.084
r_2 [Å]	1.840	1.819	1.824
r_3 [Å]	1.093	1.084	1.082
r_4 [Å]	2.075	2.111	2.059
r_5 [Å]	0.971	0.963	0.963
a_1 [deg]	110.5	110.6	110.9
a_2 [deg]	107.0	107.8	107.3
a_3 [deg]	112.4	108.4	112.8
a_4 [deg]	168.9	172.1	169.7
d_1 [deg]	120.2	120.0	120.2
ZPE [cm^{-1}]	10448	10357	10403
ω_1 [cm^{-1}]	68*i*	93*i*	66*i*
ω_2 [cm^{-1}]	63	37*i*	43
ω_3 [cm^{-1}]	185	130	152
ω_4 [cm^{-1}]	189	191	193
ω_5 [cm^{-1}]	218	199	208
ω_6 [cm^{-1}]	649	641	649
ω_7 [cm^{-1}]	947	962	954
ω_8 [cm^{-1}]	1014	1013	1012
ω_9 [cm^{-1}]	1304	1314	1326
ω_{10} [cm^{-1}]	1447	1461	1469
ω_{11} [cm^{-1}]	1447	1464	1474
ω_{12} [cm^{-1}]	3127	3108	3103
ω_{13} [cm^{-1}]	3259	3221	3219
ω_{14} [cm^{-1}]	3266	3225	3221
ω_{15} [cm^{-1}]	3781	3785	3784

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

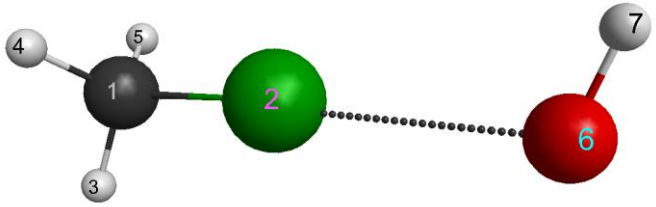


1	C						
2	H	1	r_1				
3	Y	1	r_2	2	a_1		
4	O	2	r_3	1	a_2	3	180.0
5	H	4	r_4	2	a_3	1	180.0
6	H	1	r_5	3	a_4	2	d_1
7	H	1	r_5	3	a_4	2	$-d_1$

Level[a]	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
System	**$HO^-\cdots HCH_2Cl$**	**$HO^-\cdots HCH_2Br$**	**$HO^-\cdots HCH_2I$**	**$HO^-\cdots HCH_2Cl$**	**$HO^-\cdots HCH_2Br$**	**$HO^-\cdots HCH_2I$**	**$HO^-\cdots HCH_2Cl$**	**$HO^-\cdots HCH_2Br$**	**$HO^-\cdots HCH_2I$**
Energy [E_h]	−575.088461	−531.053604	−410.200277	−575.311695	−531.273305	−410.415318	−575.358296	−531.322392	−410.455315
r_1 [Å]	1.124	1.138	1.153	1.121	1.130	1.144	1.116	1.126	1.141
r_2 [Å]	1.830	1.981	2.183	1.805	1.972	2.168	1.814	1.974	2.169
r_3 [Å]	1.769	1.714	1.652	1.756	1.709	1.649	1.764	1.717	1.654
r_4 [Å]	0.970	0.971	0.971	0.963	0.963	0.963	0.962	0.962	0.963
r_5 [Å]	1.098	1.099	1.100	1.090	1.089	1.089	1.087	1.087	1.088
a_1 [deg]	110.5	109.8	108.8	110.8	109.8	108.6	110.7	109.6	108.4
a_2 [deg]	158.7	164.4	168.5	163.7	165.6	169.7	160.8	164.4	169.2
a_3 [deg]	136.5	123.4	116.1	125.3	120.2	114.9	130.6	122.7	115.9
a_4 [deg]	105.9	105.3	104.9	106.4	105.2	104.8	106.1	105.1	104.7
d_1 [deg]	121.4	121.7	121.9	121.4	121.6	121.8	121.3	121.6	121.7
ZPE [cm^{-1}]	10409	10231	10078	10356	10188	10072	10391	10223	10063
ω_1 [cm^{-1}]	63	65	70	33	23	56	55	65	61
ω_2 [cm^{-1}]	64	69	89	69	69	104	67	67	98
ω_3 [cm^{-1}]	192	219	272	207	239	272	200	227	272
ω_4 [cm^{-1}]	245	261	282	260	272	301	256	265	284
ω_5 [cm^{-1}]	260	288	309	267	277	312	259	275	300
ω_6 [cm^{-1}]	677	575	517	676	569	509	676	566	506
ω_7 [cm^{-1}]	1038	995	939	1057	995	940	1051	996	937
ω_8 [cm^{-1}]	1051	1002	963	1064	1007	968	1056	1008	967
ω_9 [cm^{-1}]	1402	1381	1360	1427	1395	1373	1427	1396	1371
ω_{10} [cm^{-1}]	1467	1463	1461	1486	1479	1474	1490	1480	1473
ω_{11} [cm^{-1}]	1492	1490	1481	1517	1508	1503	1519	1513	1505
ω_{12} [cm^{-1}]	2743	2543	2319	2635	2505	2295	2685	2536	2309
ω_{13} [cm^{-1}]	3132	3123	3113	3083	3092	3089	3095	3099	3092
ω_{14} [cm^{-1}]	3197	3194	3189	3139	3156	3155	3153	3164	3161
ω_{15} [cm^{-1}]	3793	3793	3793	3793	3793	3794	3791	3791	3792

[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 FSMIN [Y = Cl, Br, I] front-side complexes (C_s symmetry) obtained at different levels of theory

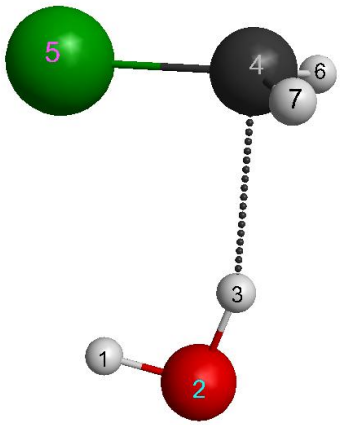


1	C						
2	Y	1	r_1				
3	H	1	r_2	2	a_1		
4	H	1	r_3	2	a_2	3	d_1
5	H	1	r_3	2	a_2	3	$-d_1$
6	O	2	r_4	1	a_3	3	0.0
7	H	6	r_5	2	a_4	3	180.0

Level[a]	**MP2/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVDZ**			**CCSD(T)-F12b/aug-cc-pVTZ**		
System	**$[CH_3\cdots Cl\cdots OH]^-$**	**$[CH_3\cdots Br\cdots OH]^-$**	**$[CH_3\cdots I\cdots OH]^-$**	**$[CH_3\cdots Cl\cdots OH]^-$**	**$[CH_3\cdots Br\cdots OH]^-$**	**$[CH_3\cdots I\cdots OH]^-$**	**$[CH_3\cdots Cl\cdots OH]^-$**	**$[CH_3\cdots Br\cdots OH]^-$**	**$[CH_3\cdots I\cdots OH]^-$**
Energy [E_h]	−575.064112	−531.042704	−410.207449	−575.289955	−531.263473	−410.423612	−575.336075	−531.312826	−410.464027
r_1 [Å]	1.806	2.024	2.274	1.782	2.015	2.257	1.797	2.016	2.256
r_2 [Å]	1.100	1.101	1.102	1.092	1.092	1.093	1.090	1.090	1.091
r_3 [Å]	1.100	1.101	1.102	1.092	1.092	1.093	1.090	1.090	1.091
r_4 [Å]	2.691	2.422	2.402	2.661	2.398	2.365	2.593	2.399	2.366
r_5 [Å]	0.973	0.972	0.972	0.965	0.964	0.963	0.964	0.964	0.963
a_1 [deg]	109.5	109.3	109.4	109.8	109.2	109.4	109.6	109.0	109.2
a_2 [deg]	109.7	109.5	109.6	110.1	109.4	109.6	109.8	109.3	109.4
a_3 [deg]	175.9	178.3	178.6	176.1	178.8	178.9	177.8	178.7	178.9
a_4 [deg]	116.5	103.2	103.9	108.5	101.7	103.7	106.3	101.6	103.5
d_1 [deg]	120.0	119.9	119.4	119.9	119.9	119.9	120.0	119.9	119.9
ZPE [cm^{-1}]	10356	10248	10166	10353	10281	10149	10349	10249	10153
ω_1 [cm^{-1}]	8	10	28*i*	25	83	77*i*	41*i*	8	33*i*
ω_2 [cm^{-1}]	100	141	142	50	141	150	117	146	146
ω_3 [cm^{-1}]	122	148	147	99	144	156	134	150	150
ω_4 [cm^{-1}]	136	205	281	153	217	280	146	218	280
ω_5 [cm^{-1}]	223	476	433	297	485	437	277	483	436
ω_6 [cm^{-1}]	709	523	625	707	533	628	689	524	625
ω_7 [cm^{-1}]	995	860	761	1023	864	758	994	863	758
ω_8 [cm^{-1}]	996	863	769	1027	869	765	994	865	767
ω_9 [cm^{-1}]	1332	1229	1164	1356	1244	1178	1349	1244	1174
ω_{10} [cm^{-1}]	1469	1453	1444	1484	1472	1461	1492	1477	1467
ω_{11} [cm^{-1}]	1469	1453	1445	1487	1473	1461	1492	1477	1467
ω_{12} [cm^{-1}]	3059	3047	3040	3025	3023	3013	3029	3026	3016
ω_{13} [cm^{-1}]	3160	3155	3151	3104	3116	3106	3112	3120	3111
ω_{14} [cm^{-1}]	3161	3156	3152	3107	3116	3107	3114	3121	3111
ω_{15} [cm^{-1}]	3772	3777	3777	3761	3780	3799	3760	3778	3797

[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 DITS [Y = F, Cl, Br, I] double-inversion transition states (C_s symmetry) obtained at different levels of theory

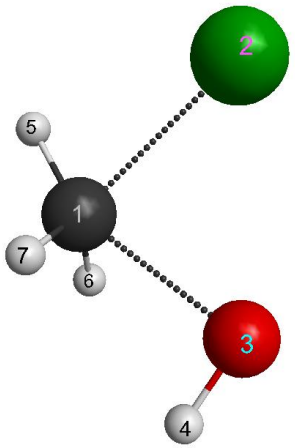


1	H						
2	O	1	r_1				
3	H	2	r_2	1	a_1		
4	C	3	r_3	2	a_2	1	0.0
5	Y	4	r_4	3	a_3	2	0.0
6	H	4	r_5	5	a_4	2	d_1
7	H	4	r_5	5	a_4	2	$-d_1$

Level[a]	MP2/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVDZ				CCSD(T)-F12b/aug-cc-pVTZ			
System	$[FCH_2\cdots HOH]^-$	$[ClCH_2\cdots HOH]^-$	$[BrCH_2\cdots HOH]^-$	$[ICH_2\cdots HOH]^-$	$[FCH_2\cdots HOH]^-$	$[ClCH_2\cdots HOH]^-$	$[BrCH_2\cdots HOH]^-$	$[ICH_2\cdots HOH]^-$	$[FCH_2\cdots HOH]^-$	$[ClCH_2\cdots HOH]^-$	$[BrCH_2\cdots HOH]^-$	$[ICH_2\cdots HOH]^-$
Energy [E_h]	−215.022786	−575.051718	−531.020094	−410.171834	−215.279804	−575.280312	−531.244345	−410.391913	−215.316518	−575.326688	−531.293366	−410.432194
r_1 [Å]	0.967	0.967	0.967	0.966	0.961	0.960	0.960	0.960	0.960	0.960	0.960	0.960
r_2 [Å]	1.009	1.009	1.009	1.007	0.996	0.996	0.996	0.994	0.996	0.996	0.996	0.993
r_3 [Å]	2.020	2.012	2.017	2.033	2.066	2.049	2.051	2.068	2.059	2.047	2.053	2.074
r_4 [Å]	1.457	1.806	1.941	2.118	1.434	1.779	1.933	2.101	1.435	1.786	1.935	2.102
r_5 [Å]	1.086	1.086	1.087	1.088	1.077	1.077	1.077	1.078	1.075	1.075	1.075	1.076
a_1 [deg]	98.9	100.0	100.4	100.8	99.1	100.1	100.6	101.1	99.1	100.2	100.5	101.0
a_2 [deg]	155.3	167.0	170.1	173.8	150.7	162.8	167.1	171.0	151.6	163.7	166.8	170.6
a_3 [deg]	82.4	89.0	90.6	93.1	81.6	88.0	90.0	92.5	81.9	88.4	89.9	92.3
a_4 [deg]	114.0	115.2	115.2	115.7	114.4	115.7	115.2	115.8	114.4	115.5	115.1	115.8
d_1 [deg]	84.8	83.4	83.5	83.2	85.6	83.9	84.3	84.0	85.5	84.2	84.5	84.1
ZPE [cm^{-1}]	10300	10144	10050	9974	10363	10178	10064	9991	10349	10155	10059	9980
ω_1 [cm^{-1}]	968*i*	859*i*	858*i*	828*i*	978*i*	851*i*	877*i*	838*i*	983*i*	864*i*	889*i*	846*i*
ω_2 [cm^{-1}]	108	96	82	73	110	102	87	74	109	97	83	77
ω_3 [cm^{-1}]	196	210	205	191	201	193	206	203	195	206	208	193
ω_4 [cm^{-1}]	213	216	214	208	217	218	214	208	217	217	215	207
ω_5 [cm^{-1}]	274	259	254	250	292	272	255	242	286	266	257	243
ω_6 [cm^{-1}]	450	485	479	469	424	459	451	445	426	443	445	442
ω_7 [cm^{-1}]	851	708	621	581	827	703	602	566	827	698	599	563
ω_8 [cm^{-1}]	908	874	869	841	929	840	839	817	923	843	839	813
ω_9 [cm^{-1}]	1069	962	917	880	1082	968	907	857	1081	960	903	853
ω_{10} [cm^{-1}]	1390	1354	1332	1313	1394	1363	1314	1299	1393	1344	1309	1290
ω_{11} [cm^{-1}]	1663	1674	1672	1670	1686	1694	1694	1694	1689	1696	1696	1694
ω_{12} [cm^{-1}]	3016	3001	3010	3048	3172	3168	3164	3170	3160	3158	3167	3171
ω_{13} [cm^{-1}]	3212	3211	3207	3198	3174	3174	3177	3203	3176	3177	3179	3210
ω_{14} [cm^{-1}]	3397	3381	3381	3368	3345	3331	3345	3333	3347	3336	3348	3334
ω_{15} [cm^{-1}]	3854	3858	3858	3859	3872	3873	3873	3873	3869	3870	3870	3870

[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 FSTS [Y = Cl, Br, I] front-side attack transition states (C_s symmetry) obtained at different levels of theory

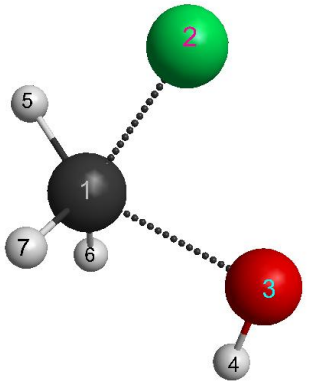


1	C						
2	Y	1	r_1				
3	O	1	r_2	2	a_1		
4	H	3	r_3	1	a_2	2	180.0
5	H	1	r_4	2	a_3	3	180.0
6	H	1	r_5	3	a_4	2	d_1
7	H	1	r_5	3	a_4	2	$-d_1$

Level[a]	MP2/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVDZ			CCSD(T)-F12b/aug-cc-pVTZ		
System	$[Cl\cdots CH_3\cdots OH]^-$	$[Br\cdots CH_3\cdots OH]^-$	$[I\cdots CH_3\cdots OH]^-$	$[Cl\cdots CH_3\cdots OH]^-$	$[Br\cdots CH_3\cdots OH]^-$	$[I\cdots CH_3\cdots OH]^-$	$[Cl\cdots CH_3\cdots OH]^-$	$[Br\cdots CH_3\cdots OH]^-$	$[I\cdots CH_3\cdots OH]^-$
Energy [E_h]	−575.016551	−530.988546	−410.141617	−575.239499	−531.209470	−410.357819	−575.286634	−531.259233	−410.398481
r_1 [Å]	2.215	2.346	2.536	2.268	2.403	2.600	2.263	2.402	2.597
r_2 [Å]	2.048	2.076	2.102	2.077	2.115	2.140	2.080	2.118	2.144
r_3 [Å]	0.976	0.976	0.977	0.969	0.969	0.970	0.968	0.968	0.969
r_4 [Å]	1.103	1.102	1.102	1.087	1.086	1.086	1.086	1.085	1.084
r_5 [Å]	1.097	1.096	1.096	1.084	1.083	1.083	1.082	1.081	1.081
a_1 [deg]	80.7	80.4	79.1	80.5	80.3	78.9	80.7	80.4	78.9
a_2 [deg]	92.9	93.6	96.6	92.6	93.3	96.5	92.4	92.9	96.2
a_3 [deg]	78.6	79.0	79.8	76.5	76.8	77.4	76.4	76.7	77.4
a_4 [deg]	81.5	81.1	81.2	79.9	79.1	79.1	79.8	79.0	79.0
d_1 [deg]	121.7	121.5	121.6	121.0	120.6	120.5	121.0	120.6	120.5
ZPE [cm^{-1}]	10439	10347	10244	10314	10238	10078	10335	10210	10119
ω_1 [cm^{-1}]	632*i*	584*i*	549*i*	639*i*	579*i*	549*i*	627*i*	578*i*	545*i*
ω_2 [cm^{-1}]	174	192	187	150	176	124	149	139	147
ω_3 [cm^{-1}]	224	207	192	185	179	153	186	169	159
ω_4 [cm^{-1}]	244	208	193	219	193	157	212	177	172
ω_5 [cm^{-1}]	450	420	386	418	386	347	420	388	350
ω_6 [cm^{-1}]	770	733	692	743	696	645	740	691	642
ω_7 [cm^{-1}]	837	810	782	798	764	730	800	761	738
ω_8 [cm^{-1}]	939	897	860	889	849	803	899	845	809
ω_9 [cm^{-1}]	1228	1201	1175	1174	1148	1115	1192	1156	1122
ω_{10} [cm^{-1}]	1434	1429	1426	1444	1441	1434	1450	1444	1441
ω_{11} [cm^{-1}]	1508	1500	1493	1499	1488	1478	1502	1490	1484
ω_{12} [cm^{-1}]	3032	3040	3046	3058	3071	3076	3060	3070	3077
ω_{13} [cm^{-1}]	3106	3119	3130	3137	3158	3169	3140	3159	3170
ω_{14} [cm^{-1}]	3204	3213	3218	3208	3224	3232	3212	3227	3233
ω_{15} [cm^{-1}]	3727	3724	3709	3706	3705	3693	3708	3705	3696

[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 S11. 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	O	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]	−214.990402	−215.239070	−215.276335
r_1 [Å]	1.749	1.748	1.753
r_2 [Å]	1.916	1.911	1.917
r_3 [Å]	0.974	0.966	0.966
r_4 [Å]	1.116	1.104	1.101
r_5 [Å]	1.117	1.106	1.103
r_6 [Å]	1.096	1.085	1.083
a_1 [deg]	79.7	79.7	79.7
a_2 [deg]	94.6	95.8	95.6
a_3 [deg]	80.3	79.9	79.7
a_4 [deg]	80.9	80.4	80.1
a_5 [deg]	94.7	95.0	94.8
d_1 [deg]	−175.1	−174.7	−174.8
d_2 [deg]	−160.4	−159.0	−159.1
d_3 [deg]	146.8	148.2	148.0
d_4 [deg]	−103.2	−101.9	−101.8
ZPE [cm^{-1}]	10715	10680	10667
ω_1 [cm^{-1}]	673*i*	731*i*	729*i*
ω_2 [cm^{-1}]	255	245	227
ω_3 [cm^{-1}]	276	262	247
ω_4 [cm^{-1}]	356	343	335
ω_5 [cm^{-1}]	561	540	538
ω_6 [cm^{-1}]	912	920	916
ω_7 [cm^{-1}]	958	967	957
ω_8 [cm^{-1}]	1128	1133	1126
ω_9 [cm^{-1}]	1312	1318	1317
ω_{10} [cm^{-1}]	1418	1427	1431
ω_{11} [cm^{-1}]	1566	1571	1570
ω_{12} [cm^{-1}]	2864	2850	2869
ω_{13} [cm^{-1}]	2903	2891	2901
ω_{14} [cm^{-1}]	3179	3160	3167
ω_{15} [cm^{-1}]	3741	3735	3734