Table S1. Effect of Basis Set and Frozen Core Model on the MP2 C_{3v} Stationary Point Geometries and Energies[a]

	$R_{C\text{-}F}$	$R_{C\text{-}I}$	$R_{C\text{-}H}$	∠I-C-H	Energy
			$F^- + CH_3I$		
ECP/d	∞	2.143	1.094	108.0	0
ECP/d/fc	∞	2.145	1.096	108.0	0
PP/d	∞	2.149	1.095	107.7	0
ECP/t	∞	2.112	1.079	108.3	0
PP/t	∞	2.117	1.080	107.9	0
Expt	∞	2.132[b]	1.084	107.7	0
			F^----CH_3I		
ECP/d	2.433	2.228	1.088	105.9	-68.2 (-67.4)
ECP/d/fc	2.435	2.228	1.089	105.9	-67.8 (-66.9)
PP/d	2.424	2.234	1.088	105.8	-69.0 (-68.2)
ECP/t	2.489	2.167	1.074	107.6	-65.7 (-64.9)
PP/t	2.419	2.185	1.074	106.4	-69.0 (-68.2)
			$[F\text{--}CH_3\text{--}I]^-$ TS		
ECP/d	2.153	2.375	1.083	99.5	-65.3 (-64.4)
ECP/d/fc	2.155	2.376	1.084	99.5	-65.3 (-64.4)
PP/d	2.150	2.377	1.083	99.4	-66.5 (-66.1)
ECP/t	2.064	2.381	1.067	98.0	-56.5 (-55.6)
PP/t	2.068	2.371	1.068	98.1	-63.6 (-62.3)
			FCH_3---I^-		
ECP/d	1.433	3.585	1.094	71.5	-208.8 (-200.4)
ECP/d/fc	1.435	3.584	1.095	71.5	-207.5 (-199.2)
PP/d	1.433	3.577	1.094	71.5	-211.7 (-203.3)
ECP/t	1.406	3.598	1.080	70.9	-210.5 (-202.1)
PP/t	1.410	3.522	1.082	71.1	-208.8 (-200.4)
			$FCH_3 + I^-$		
ECP/d	1.407	∞	1.097	71.7	-172.4 (-164.8)
ECP/d/fc	1.409	∞	1.098	71.7	-171.1 (-163.6)
PP/d	1.407	∞	1.097	71.7	-174.9 (-167.8)
ECP/t	1.382	∞	1.083	71.2	-175.3 (-167.4)
PP/t	1.385	∞	1.085	71.3	-171.1 (-163.6)
Expt	1.382[b]	∞	1.095	71.5	-197.1 (-188.7)[c]

[a]Bond lengths are in angstroms (Å), and angles are in degrees. Energies in kJ/mol are with respect to the F^- + CH_3I reactants, and are at 0 K and do not include zero-point energy (ZPE). The values in parentheses include ZPE.

[b]The experimental geometries of CH_3I and CH_3Cl are from ref 85.

[c]The reaction exothermicity at 0 K without ZPE calculated from standard molar enthalpies of formation in ref. 88 and frequency data in refs. 86 and 87. The values in parentheses include ZPE.

Table S2. Effect of Basis Set and Frozen Core Model on the MP2 C_s Stationary Point Geometries and Energies[a]

	$R_{C\text{-}F}$	$R_{C\text{-}I}$	$R_{F\text{-}H1}$	$R_{C\text{-}H1}$	∠F-C-I	∠H2-C-H1	Energy
				F^- ---HCH_2I			
ECP/d	2.712	2.169	1.574	1.147	115.4	113.2	-79.1 (-79.5)
ECP/d/fc	2.714	2.169	1.576	1.148	115.4	113.2	-79.1 (-79.1)
PP/d	2.711	2.174	1.574	1.146	115.7	113.3	-79.5 (-79.9)
ECP/t	2.680	2.130	1.550	1.136	114.8	112.5	-79.9 (-79.9)
PP/t	2.691	2.135	1.566	1.133	115.3	112.8	-82.0 (-82.0)
				$[F\text{--}HCH_2\text{--}I]^-$ TS			
ECP/d	2.574	2.195	2.049	1.092	160.4	111.0	-66.1 (-66.1)
ECP/d/fc	2.575	2.196	2.052	1.093	160.5	111.0	-66.1 (-66.1)
PP/d	2.568	2.201	2.045	1.092	160.4	111.1	-67.4 (-67.4)
ECP/t	2.556	2.153	2.090	1.076	163.6	110.2	-64.9 (-64.4)
PP/t	2.538	2.161	2.046	1.078	161.7	110.7	-67.4 (-67.4)

[a]Bond lengths are in angstroms (Å), and angles are in degrees. Energies in kJ/mol are with respect to the F^- + CH_3I reactants, and are at 0 K and do not include zero-point energy (ZPE). The values in parentheses include ZPE.

Table S3. Effect of Basis Set and Frozen Core Model on the MP2 C_{3v} Stationary Point Frequencies.[a]

mode	ECP/d	ECP/d/fc	PP/d	ECP/t	PP/t	Expt[b]
		CH_3I				
A_1 C-I str	551	550	558	587	584	539
E CH_3 rock	910	907	900	917	913	901
A_1 CH_3 deform	1290	1285	1284	1322	1310	1276
E CH_3 deform	1469	1461	1457	1496	1497	1465
A_1 C-H str	3112	3106	3115	3136	3137	3080
E C-H str	3238	3230	3243	3230	3235	3188
		CH_3F				
A_1 C-F str	1039	1036	1039	1089	1079	1078
E CH_3 rock	1189	1186	1189	1222	1219	1204
A_1 CH_3 deform	1473	1470	1473	1518	1513	1496
E CH_3 deform	1492	1490	1492	1537	1541	1515
A_1 C-H str	3095	3090	3095	3107	3104	3075
E C-H str	3209	3203	3209	3192	3190	3147
		F^----CH_3I				
E F^- bend	103	102	103	83	100	
A_1 F-C str	158	157	156	156	166	
A_1 C-I str	379	378	380	463	430	
E CH_3 rock	850	849	852	868	865	
A_1 CH_3 deform	1151	1149	1147	1212	1188	
E CH_3 deform	1418	1416	1415	1464	1460	
A_1 C-H str	3177	3172	3178	3196	3197	
E C-H str	3332	3327	3335	3309	3318	
		$[F$--CH_3--$I]^-$ TS				
E F-C-I bend	186	186	186	207	209	
A_1 F-C-I str	230	230	231	237	239	

E CH_3 rock	900	898	902	938	944
A_1 out-of-plane bend	1074	1072	1070	1083	1090
E CH_3 deform	1404	1403	1402	1429	1433
A_1 C-H str	3202	3197	3202	3230	3224
E C-H str	3397	3391	3397	3399	3391
reaction coordinate	331*i*	330*i*	334*i*	439*i*	400*i*
		FCH_3---I^-			
E I^- bend	89	89	94	82	86
A_1 C-I str	79	79	83	77	83
A_1 F-C str	958	954	958	1011	995
E CH_3 rock	1154	1151	1156	1186	1180
A_1 CH_3 deform	1433	1429	1433	1473	1464
E CH_3 deform	1479	1477	1479	1521	1525
A_1 C-H str	3124	3120	3124	3135	3134
E C-H str	3252	3246	3251	3232	3230

[a]Frequencies are in units of cm^{-1}.

[b]The experimental frequencies of CH_3I and CH_3F are from refs. 86 and 87, respectively.

Table S4. Effect of Basis Set and Frozen Core Model on the MP2 C_s Stationary Point Frequencies.[a]

mode	ECP/d	ECP/d/fc	PP/d	ECP/t	PP/t
		F^- ---HCH_2I			
A' F^- bend	77	76	76	82	76
A' F-C str	291	289	290	293	287
A" CH_3 torsion	311	310	310	336	314
A' C-I str	515	514	520	551	550
A" CH_3 rock	939	938	942	964	955
A' CH_3 rock	942	941	943	968	959
A' CH_3 deform	1344	1341	1344	1392	1374
	1451	1449	1447	1489	1480
A" CH_3 deform	1505	1502	1501	1549	1546
A' C-H str	2430	2426	2436	2347	2411
	3124	3119	3126	3135	3135
A" C-H str	3196	3190	3199	3192	3199
		$[F\text{--}HCH_2\text{--}I]^-$ TS			
A" CH_3 torsion	111	110	112	113	113
A' F-C str	165	163	165	160	167
A' C-I str	460	459	465	499	494
A' CH_3 rock	767	766	770	799	787
A" CH_3 rock	886	884	889	908	897
A' CH_3 deform	1185	1183	1185	1227	1211
	1425	1423	1423	1464	1462
A" CH_3 deform	1431	1429	1430	1474	1471
A' C-H str	3142	3137	3143	3173	3167
	3283	3278	3287	3280	3277
A" C-H str	3287	3281	3290	3281	3281
A' F bend	110*i*	110*i*	109*i*	93*i*	109*i*

[a]Frequencies are in units of cm^{-1}.

Table S5. Comparison of Complex and Transition State Geometries for MP2 and Different DFT Functionals[a]

	$R_{C\text{-}F}$	$R_{C\text{-}I}$	$R_{C\text{-}H}$	∠I-C-H
		FCH_3---I^-		
MP2	1.433	3.585	1.094	71.5
	1.406	3.598	1.080	70.9
OPBE	1.412	4.171	1.099	71.1
	1.400	4.257	1.095	70.7
OLYP	1.427	4.093	1.099	71.4
	1.415	4.176	1.093	71.1
BhandH	1.400	3.724	1.095	71.0
	1.387	3.741	1.088	70.7
HCTH407	1.421	3.927	1.096	71.2
	1.410	3.982	1.090	71.0
B97-1	1.424	3.720	1.096	71.4
	1.411	3.738	1.089	71.0

	$R_{C\text{-}F}$	$R_{C\text{-}I}$	$R_{F\text{-}H1}$	$R_{C\text{-}H1}$	∠F-C-I	∠H2-C-H1
			F^- ---HCH_2I			
MP2	2.712	2.169	1.574	1.147	115.4	113.2
	2.680	2.130	1.550	1.136	114.8	112.5
OPBE	2.638	2.184	1.475	1.182	121.6	112.9
	2.635	2.159	1.474	1.178	120.8	112.7
OLYP	2.704	2.210	1.580	1.153	122.7	112.9
	2.717	2.183	1.602	1.143	122.0	112.6
BhandH	2.660	2.183	1.511	1.158	116.3	113.5
	2.662	2.157	1.524	1.148	115.9	113.1
HCTH407	2.701	2.201	1.581	1.147	121.9	112.9
	2.711	2.176	1.597	1.139	121.0	112.7
B97-1	2.675	2.200	1.529	1.161	118.2	113.4
	2.683	2.171	1.548	1.149	117.6	113.1
			$[F\text{--}HCH_2\text{--}I]^-$ TS			
MP2	2.574	2.195	2.049	1.092	160.4	111.0

	2.556	2.153	2.090	1.076	163.6	110.2
OPBE	2.552	2.244	1.985	1.097	158.7	111.9
	2.589	2.207	2.031	1.090	159.2	111.5
OLYP	2.613	2.264	1.991	1.096	155.8	112.0
	2.636	2.232	2.043	1.088	157.0	111.8
BhandH	2.509	2.221	1.958	1.092	158.9	111.3
	2.525	2.190	1.996	1.083	160.0	110.9
HCTH407	2.604	2.252	1.975	1.094	155.4	111.9
	2.621	2.222	2.019	1.086	156.6	111.6
B97-1	2.532	2.256	1.914	1.096	155.8	111.9
	2.551	2.219	1.956	1.087	156.9	111.4

[a]Bond lengths are in angstroms (Å), and angles are in degrees. The upper values were calculated using the ECP/d basis set and the lower values were calculated using the ECP/t basis set.

Table S6. Comparison of MP2 and DFT Harmonic Frequencies of Stationary Points for the $F^- + CH_3I \rightarrow CH_3F + I^-$ PES[a]

mode	MP2	OPBE	OLYP	BhandH	HCTH407	B97-1	Expt[b]
			CH_3I				
A_1 C-I str	551	543	517	549	529	516	539
	587	560	532	565	543	534	
E CH_3 rock	910	870	870	910	876	887	901
	917	878	881	921	884	899	
A_1 CH_3 deform	1290	1219	1223	1285	1229	1256	1276
	1322	1238	1248	1312	1253	1284	
E CH_3 deform	1469	1391	1398	1456	1402	1429	1465
	1496	1421	1434	1490	1436	1468	
A_1 C-H str	3112	3052	3046	3121	3071	3072	3080
	3136	3052	3044	3119	3067	3071	
E C-H str	3238	3189	3172	3245	3203	3191	3188
	3230	3173	3155	3232	3185	3177	
			CH_3F				
A_1 C-F str	1039	1050	1009	1110	1021	1038	1078
	1089	1067	1025	1133	1036	1059	
E CH_3 rock	1189	1152	1147	1206	1154	1173	1204
	1222	1165	1164	1228	1171	1195	
A_1 CH_3 deform	1473	1414	1413	1482	1420	1446	1496
	1518	1439	1445	1515	1450	1481	
E CH_3 deform	1492	1422	1423	1487	1428	1457	1515
	1537	1446	1455	1517	1460	1491	
A_1 C-H str	3095	2998	2993	3080	3015	3029	3075
	3107	2982	2978	3069	3000	3019	
E C-H str	3209	3109	3094	3180	3120	3127	3147
	3192	3075	3064	3155	3090	3103	

			FCH_3---I^-			
E I^- bend	89	53	57	80	59	76
	82	48	54	79	67	72
A_1 C-I str	79	40	45	68	56	68
	77	40	44	66	57	66
A_1 F-C str	958	987	936	1033	941	950
	1011	1008	957	1058	960	973
E CH_3 rock	1154	1127	1120	1176	1120	1136
	1186	1140	1136	1197	1141	1155
A_1 CH_3 deform	1433	1395	1395	1448	1391	1408
	1473	1422	1425	1478	1425	1442
E CH_3 deform	1479	1421	1422	1478	1423	1448
	1521	1445	1451	1508	1454	1482
A_1 C-H str	3124	3026	3024	3110	3044	3063
	3135	3013	3009	3098	3030	3048
E C-H str	3252	3150	3138	3222	3162	3173
	3232	3114	3106	3195	3131	3145
			F^- ---HCH_2I			
A' F- bend	77	87	78	81	76	77
	82	89	79	82	77	78
A' F-C str	291	290	254	312	261	297
	293	279	240	303	248	282
A" CH_3 torsion	311	329	304	321	299	312
	336	339	308	326	303	317
A' C-I str	515	476	442	479	461	436
	551	499	465	504	480	466
A" CH_3 rock	939	872	867	944	878	909
	964	887	888	964	896	930
A' CH_3 rock	942	912	898	949	903	920

	968	925	912	965	917	937
A' CH_3 deform	1344,1451	1264,1375	1254,1378	1344,1445	1264,1383	1298,1411
	1392,1489	1283,1399	1280,1412	1374,1474	1289,1414	1329,1446
A" CH_3 deform	1505	1422	1421	1506	1427	1461
	1549	1452	1459	1540	1464	1499
A' C-H str	2430,3124	2039,3036	2329,3044	2273,3131	2384,3072	2246,3072
	2347,3135	2001,3037	2358,3044	2286,3127	2387,3069	2268,3070
A" C-H str	3196	3120	3119	3204	3152	3142
	3192	3112	3112	3195	3140	3136
			$[F\text{--}HCH_2\text{--}I]^-$ TS			
A" CH_3 torsion	111	139	140	124	143	142
	113	130	130	119	133	136
A' F-C str	165	149	149	181	155	179
	160	140	141	176	149	172
A' C-I str	460	371	357	401	371	352
	499	404	380	433	397	383
A' CH_3 rock	767	649	671	746	676	682
	799	679	703	775	706	709
A" CH_3 rock	886	832	840	890	846	861
	908	845	849	905	856	877
A' CH_3 deform	1185,1425	1087,1353	1108,1366	1165,1414	1119,1366	1125,1388
	1227,1464	1119,1388	1141,1403	1203,1452	1148,1404	1166,1430
A" CH_3 deform	1431	1357	1371	1426	1375	1398
	1474	1394	1411	1464	1413	1441
A' C-H str	3142,3283	3060,3217	3049,3196	3146,3289	3066,3218	3074,3214
	3173,3280	3066,3201	3059,3189	3149,3277	3075,3208	3080,3204
A" C-H str	3287	3236	3213	3302	3239	3239
	3281	3217	3199	3285	3222	3226
reaction coordinate	110*i*	140*i*	118*i*	135*i*	118*i*	148*i*
	93*i*	123*i*	108*i*	121*i*	109*i*	138*i*

[a]Frequencies are in units of cm^{-1}. Upper values were calculated using the ECP/d basis set and the lower values were calculated using the ECP/t basis set.

[b]The experimental frequencies of CH_3I and CH_3F are from refs. 86 and 87, respectively.