Quantum Chemical Calculations of the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ Potential Energy Surface†

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Electronic structure theory calculations, using MP2 theory and the DFT functionals OPBE, OLYP, HCTH407, BhandH, and B97-1, were performed to characterize the structures, vibrational frequencies, and energies for stationary points on the $Cl^- + CH_3I \rightarrow ClCH_3 + I^-$ potential energy surface. The aug-cc-pVDZ and aug-cc-pVTZ basis sets, with an effective core potential (ECP) for iodine, were employed. Single-point CCSD(T) calculations were performed to obtain the complete basis set (CBS) limit for the reaction energies. DFT was found to give significantly longer halide ion/carbon atom bond lengths for the ion−dipole complexes and central barrier transition state than MP2. BhandH, with either the aug-cc-pVDZ or aug-cc-pVTZ basis sets, gives good agreement with the experimental structures for both CH_3I and CH_3Cl. The frequencies of CH_3I and CH_3Cl, obtained with the different levels of theory and basis sets, are in excellent agreement with experiment. The major difference between the MP2 and DFT frequencies is for the imaginary frequency of the central barrier. Using the aug-cc-pVTZ basis the MP2 value for this frequency ranges from 1.26 to 1.59 times larger than those for the DFT functionals. Thus, the MP2 and DFT theories have different PES shapes in the vicinity of the $[Cl\text{--}CH_3\text{--}I]^-$ central barrier. The CCSD(T)/CBS energies are in good agreement with experiments for the complexation energies and reaction exothermicity, with a small 1 kcal/mol difference for the latter. The CCSD(T)/CBS central barrier height is lower than values deduced by using statistical theoretical models to fit the $Cl^- + CH_3I \rightarrow ClCH_3 + I^-$ experimental rate constant, which is consistent with the expected nonstatistical dynamics for the reaction. The BhandH energies are in overall best agreement with the CCSD(T) values, with a largest difference of only 0.7 kcal/mol.

I. Introduction

There is considerable interest in understanding the atomic-level dynamics of gas-phase bimolecular nucleophilic substitution (S_N2) reactions of the type[1−10]

$$X^- + CH_3Y \rightarrow XCH_3 + Y^- \qquad (1)$$

These reactions are of central importance in gas-phase ion chemistry and organic reaction mechanisms.[11] Studies of these reactions in the gas phase have provided the opportunity to probe the intrinsic reaction mechanism without solvent,[12] and it is well-known that the reactions proceed via a double-well potential. The two wells correspond to loose ion−dipole complexes, i.e., the pre- and postreaction complexes $X^-\text{---}CH_3Y$ and $XCH_3\text{---}Y^-$, which are separated by a $[X\text{--}CH_3\text{--}Y]^-$ central barrier. The energy profile for the $Cl^- + CH_3I \rightarrow ClCH_3 + I^-$ reaction is shown in Figure 1. This potential model has been confirmed by numerous theoretical and experimental studies,[13−16] including a structural characterization of a S_N2 ion−dipole complex.[17,18]

For the first proposed mechanism of the gas-phase $X^- + CH_3Y$ reaction, it is assumed that the reaction system becomes trapped in the $X^-\text{---}CH_3Y$ and $XCH_3\text{---}Y^-$ complexes with complete randomization of their vibrational energies.[2] An ion−molecule capture theoretical model, such as classical trajectories[19] or variational transition state,[20] is used to calculate the $X^- + CH_3Y \rightarrow X^-\text{---}CH_3Y$ association rate constant and RRKM theory is used to calculate the unimolecular lifetime of each complex and the branching ratio for its two unimolecular

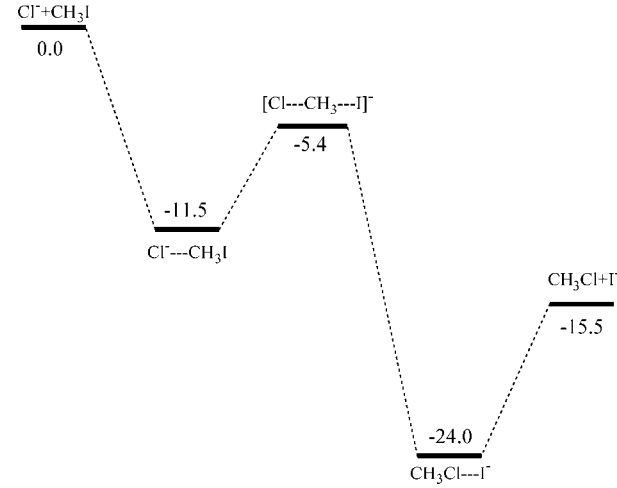

Figure 1. Schematic energy profile for the $Cl^- + CH_3I \rightarrow ClCH_3 + I^-$ reaction at the CCSD(T)/CBS level of theory. The energies shown are in kcal/mol and are relative to the $Cl^- + CH_3I$ reactants. Zero-point energies are not included.

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pathways,[21] e.g., X^----$CH_3Y \rightarrow X^- + CH_3Y$ and X^----$CH_3Y \rightarrow XCH_3$---Y^-. This model predicts that if one of the transition states (TSs), i.e., the one at the central barrier or either the $X^- + CH_3Y$ or $XCH_3 + Y^-$ variational TS, has a sum of states (or free energy) much smaller than those of the other two, the S_N2 rate constant is determined by properties of this TS and given by transition state theory.[22]

Both experimental[23−31] and computational[32−44] studies have shown that this model mechanism does not characterize all $X^- + CH_3Y$ S_N2 reactions. Due to inefficient energy transfer between $X^- + CH_3Y$ relative translation and CH_3Y rotation and vibration, the $X^- + CH_3Y \rightarrow X^-$---$CH_3Y$ association rate constant may be smaller than that of the capture model.[34,36] Energy randomization may be incomplete for the X^----CH_3Y prereaction complex[24,26,29,30,33,34,37−39] and for a highly exothermic S_N2 reaction the reaction system may move directly from the $[X$--CH_3--$Y]^-$ central barrier to products without forming the XCH_3---Y^- postreaction complex.[31,43,44] Upon C−Y stretch vibrational or $X^- + CH_3Y$ translational activation, the mechanism may become direct without forming either the X^----CH_3Y or XCH_3---Y^- complex.[27,28,32,34,40,41,43,44] In chemical dynamics simulations of the $Cl^- + CH_3Cl$ and $Cl^- + CH_3Br$ S_N2 reactions extensive recrossings of the central barrier are observed[35,37,42] in contrast to the prediction of RRKM theory that there should be negligible recrossings. Quantum dynamics calculations are in agreement with the above results, and illustrate the important role of resonances in S_N2 reactions.[45−50]

Interpreting the dynamics and kinetics of S_N2 reactions, by either theoretical calculations or chemical dynamics simulations,[51,52] requires accurate potential energy surfaces (PES's). G2(+) theory has been used to calculate energetics for the reactions $X^- + CH_3X \rightarrow XCH_3 + X^-$ and $X^- + CH_3Y \rightarrow XCH_3 + Y^-$, X, Y = F, Cl, Br, and I.[53−55] Density functional theory (DFT) and ab initio methods have been compared for calculating $X^- + CH_3X \rightarrow XCH_3 + X^-$ (X = F, Cl, Br, I) PESs.[56−58] A range of DFT methods have been compared for $X^- + CH_3Y \rightarrow XCH_3 + Y^-$ (X, Y = F, Cl, Br) S_N2 reactions.[59] DFT models have been assessed for the $CH_3X + F^-$ (X = F, Cl, CN, OH, SH, NH_2, PH_2) reactions[60] and a range of ab initio and DFT methods have been used to analyze the $X^- + CH_3X$ (X = F, Cl, CN, OH, SH, NH_2, PH_2) S_N2 reactions.[61] Recently, Bickelhaupt and co-workers carried out a detailed evaluation of the performance of many DFT functionals for describing PES's of a wide range of S_N2 reactions.[62] Analytics PES's and ab initio PES's for direct dynamics have been used in studies of the $Cl^- + CH_3Cl$,[35,42,63−65] $Cl^- + CH_3Br$,[38,66] $F^- + CH_3Cl$,[41,67] $F^- + CH_3OH$,[43] and $Cl^- + CH_3I$[31] S_N2 reactions. High-level CCSD(T) ab initio calculations have provided properties for the $F^- + CH_3Cl$,[67,68] $F^- + CH_3F$,[69] $Cl^- + CH_3Cl$,[70] $X^- + CH_3Y \rightarrow XCH_3 + Y^-$ (X, Y = F, Cl, Br),[59] $CH_3X + F^-$ (X = F, Cl, CN, OH, SH, NH_2, PH_2),[60] $OH^- + CH_{(4-n)}Cl_n$ (n = 1−4),[71] and $CH_3X + X^-$ (X = F, Cl, CN, OH, SH, NH_2, PH_2) S_N2 reactions.[61]

In recent work a direct chemical dynamics simulation,[31] at the MP2(fc)/ECP/aug-cc-pVDZ level of theory, was used to study the dynamics of the $Cl^- + CH_3I$ S_N2 reaction and compare with results of ion imaging experiments. To investigate the adequacy of these MP2 direct dynamics, it is of interest to compare properties of the $Cl^- + CH_3I \rightarrow ClCH_3 + I^-$ PES, given by the above MP2 method and other electronic structure theoretical methods. In the work presented here, stationary point properties of the $Cl^- + CH_3I$ S_N2 reaction are calculated by using the DFT, MP2, and CCSD(T) theories with different basis sets and DFT functionals. Comparisons are made between the results of these calculations and with experimental and previously obtained theoretical results.

II. Computational Procedure

All calculations were carried out with the NWChem program.[72] MP2[73,74] and DFT,[62,75−78] with the OPBE, OLYP, HCTH407, BhandH, and B97-1 functionals, were used to calculate the energies, geometries, and frequencies of the stationary points for the reactants, ion−dipole complexes, transition state, and products on the $Cl^- + CH_3I \rightarrow ClCH_3 + I^-$ PES. Three different basis sets were employed for the calculations. For the ECP/6-31+G(d) basis, the 6-31+G(d) basis[79] was used for the C, H, and Cl atoms and, for iodine, the Wadt and Hay effective core potential (ECP) was used for the core electrons and an uncontracted 3s3p basis set for the valence electrons.[80] This iodine basis set was augmented by a d-polarization function with a 0.262 exponent, and s, p, and d diffuse functions with exponents of 0.034, 0.039, and 0.0873, respectively.[81] For the basis sets identified as ECP/d and ECP/t, the double- (d) and triple-ζ (t) basis sets, aug-cc-pVDZ and aug-cc-pVTZ,[82] were used for the C, H, and Cl atoms. In addition, for the ECP/t basis the above iodine basis was further augmented by an f-polarization function with a 0.52 exponent.[83]

Structures, frequencies, and energies were calculated at the MP2 level of theory with each of the above three basis sets and at the DFT level of theory with only the ECP/d and ECP/t basis sets. The frozen core (fc) orbital method was used for MP2 calculations. The stationary nature of structures was confirmed by harmonic vibrational frequency calculations, that is, the potential minima possess all real frequencies, whereas the transition state possesses only one imaginary frequency. The harmonic zero-point energy (ZPE) was obtained at all these levels of theory.

To obtain more reliable energies, higher level single-point energy calculations were performed at the CCSD(T) level of theory.[84] The frozen core (fc) orbital method was used, as for the above MP2 calculations. The calculations were performed with the correlation consistent Gaussian basis sets, as above, denoted by aug-cc-pVXZ, where X is the cardinal number for the basis set (X = D, T, Q, and 5).[82] The results were extrapolated to the complete basis set (CBS) limit.[85] For the C, H, and Cl atoms the aug-cc-pVXZ basis was used. For iodine the Peterson aug-cc-pVXZ basis, with a pseudopotential (PP),[86] was used. Only the 5s5p orbitals were correlated for I, which is consistent with the correlation for other atoms, i.e. 2s2p for C, 3s3p for Cl, and 1s for H. Following the terminology used above, for the MP2 and DFT calculations, these basis sets are identified as PP/x, where x = d, t, q, and 5. These CCSD(T) calculations are based on MP2/PP/d minimum geometries, which are very close to MP2/ECP/d geometry. The largest differences between these two geometries are 0.023 Å for the C---I^- bond of the $ClCH_3$---I^- complex and 0.28° for the I−C−H and Cl−C−H angles of the transition state.

III. Results and Discussion

The geometries, harmonic vibrational frequencies, and relative energies determined from the electronic structure calculations are discussed in the following, and summarized in Tables 1−4 and Figures 1 and 2.

A. Geometries. The stationary point geometries are listed in Table 1 and depicted in Figure 2. The MP2 and MP2(fc) geometries are quite similar, with the bond distance and angle deviations less than 0.023 Å and 0.14°, respectively, illustrating

TABLE 1: Geometries of Stationary Points for the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ Reaction[a]

	R_{C-Cl}	R_{C-I}	R_{C-H}	∠I−C−H	∠Cl−C−H	∠H−C−H
			$Cl^- + CH_3I$ reactants			
MP2		2.143[b](2.145)[d]	1.094(1.096)	107.98(107.97)		110.91(110.92)
		2.115[c](2.117)	1.079(1.083)	107.87(107.89)		111.02(111.00)
OPBE		2.139	1.097	107.85		111.05
		2.124	1.091	107.84		111.06
OLYP		2.158	1.096	107.79		111.10
		2.143	1.089	107.72		111.16
BhandH		2.140	1.093	107.84		111.05
		2.126	1.084	107.88		111.01
HCTH407		2.155	1.093	107.72		111.16
		2.140	1.086	107.66		111.22
B97-1		2.147	1.095	108.00		110.90
		2.133	1.086	107.83		111.06
expt[e]		2.132	1.084	107.7		111.2
			Cl^----CH_3I complex			
MP2	3.068(3.091)	2.186 (2.185)	1.090(1.092)	107.43(107.55)	72.45(72.48)	111.44(111.32)
	3.047(3.068)	2.149 (2.151)	1.076(1.080)	107.72(107.77)	72.12(72.08)	111.17(111.12)
OPBE	3.234	2.196	1.093	107.24	72.76	111.61
	3.267	2.172	1.087	107.43	72.57	111.44
OLYP	3.239	2.228	1.092	106.79	73.21	112.01
	3.282	2.199	1.085	107.00	73.00	111.83
BhandH	3.092	2.193	1.089	107.28	72.72	111.57
	3.107	2.170	1.081	107.54	72.46	111.33
HCTH407	3.176	2.223	1.089	106.81	73.19	112.00
	3.213	2.196	1.082	107.07	72.93	111.76
B97-1	3.061	2.229	1.090	106.69	73.31	112.11
	3.080	2.198	1.082	107.00	73.00	111.82
			$[Cl\text{--}CH_3\text{--}I]^-$ saddle point			
MP2	2.383(2.384)	2.582 (2.588)	1.081(1.082)	92.20(92.10)	87.80(87.90)	119.85(119.87)
	2.326(2.327)	2.554 (2.559)	1.067(1.070)	91.61(91.47)	88.39(88.53)	119.92(119.93)
OPBE	2.426	2.574	1.085	93.26	86.74	119.68
	2.398	2.557	1.079	92.82	87.18	119.76
OLYP	2.476	2.632	1.083	92.92	87.08	119.74
	2.444	2.621	1.076	92.44	87.56	119.82
BhandH	2.449	2.584	1.080	93.41	86.59	119.65
	2.425	2.577	1.071	93.02	86.98	119.72
HCTH407	2.483	2.633	1.081	93.03	86.97	119.72
	2.444	2.628	1.073	92.31	87.69	119.84
B97-1	2.462	2.603	1.082	93.33	86.67	119.67
	2.436	2.595	1.073	92.89	87.11	119.75
			$ClCH_3$---I^- complex			
MP2	1.824(1.827)	3.535 (3.540)	1.091(1.093)	71.90(71.76)	108.26(108.30)	110.64(110.62)
	1.802(1.808)	3.491 (3.491)	1.077(1.081)	71.48(71.50)	108.52(108.44)	110.40(110.49)
OPBE	1.801	4.017	1.095	71.34	108.68	110.24
	1.793	4.062	1.090	71.25	108.79	110.15
OLYP	1.830	3.954	1.094	71.78	108.23	110.68
	1.820	4.006	1.088	71.67	108.33	110.59
BhandH	1.816	3.653	1.091	71.66	108.37	110.55
	1.805	3.669	1.083	71.42	108.57	110.36
HCTH407	1.816	3.838	1.092	71.30	108.58	110.35
	1.806	3.874	1.086	71.38	108.62	110.31
B97-1	1.848	3.613	1.092	72.21	107.80	111.08
	1.836	3.631	1.084	72.22	107.96	110.92
			$ClCH_3 + I^-$ products			
MP2	1.794(1.797)		1.094(1.096)		108.29(108.27)	110.63(110.64)
	1.774(1.780)		1.080(1.084)		108.39(108.36)	110.53(110.57)
OPBE	1.778		1.098		108.63	110.30
	1.771		1.093		108.73	110.21
OLYP	1.800		1.097		108.35	110.57
	1.794		1.091		108.37	110.55
BhandH	1.787		1.094		108.32	110.60
	1.777		1.086		108.50	110.43
HCTH407	1.785		1.095		108.58	110.35
	1.778		1.088		108.66	110.27
B97-1	1.810		1.095		107.97	110.93
	1.800		1.087		108.13	110.78
expt[e]	1.785		1.090		108.1	110.8

[a] Bond lengths are in angstroms (Å), and angles are in deg. [b] Upper values are calculated with the ECP/d basis set. [c] Lower values are calculated with the ECP/t basis set. [d] Values in parentheses are calculated at the MP2 theory with the frozen core orbital method (fc). [e] The experimental geometries of CH_3I and CH_3Cl are from ref 87.

the accuracy of the frozen core (fc) approximation. For the MP2 and different DFT functionals the structures given by the ECP/d and ECP/t basis sets are similar. However, the latter gives shorter bond lengths for each of the stationary points, except for the Cl^----C and C---I^- bonds of the complexes. For these bonds, ECP/d gives shorter bond lengths when used with DFT. The difference in the ECP/d and ECP/t values for the carbon−halogen bond lengths is largest and 0.052 Å for the C---I^- bond of

TABLE 2: Harmonic Frequencies of Stationary Points for the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ Reaction[a]

mode	MP2	OPBE	OLYP	BhandH	HCTH407	B97-1	expt[e]
			CH_3I				
A_1 C−I str	551[c](550)	543	517	549	529	516	539
	579[b](576)[d]	557	530	564	540	532	
E CH_3 rock	910(907)	870	870	910	876	887	901
	924(917)	875	878	919	883	897	
A_1 CH_3 deform	1290(1285)	1219	1223	1285	1229	1256	1276
	1318(1305)	1238	1249	1309	1253	1282	
E CH_3 deform	1469(1461)	1391	1398	1456	1402	1429	1465
	1495(1492)	1419	1433	1488	1436	1467	
A_1 C−H str	3112(3106)	3052	3046	3121	3071	3072	3080
	3166(3116)	3048	3042	3177	3065	3070	
E C−H str	3238(3230)	3189	3172	3245	3203	3191	3188
	3249(3236)	3169	3153	3230	3182	3177	
			CH_3Cl				
A_1 C−Cl str	754(752)	755	714	760	726	724	740
	776(767)	756	714	764	728	726	
E CH_3 rock	1033(1031)	990	989	1035	999	1003	1038
	1058(1047)	1004	1005	1054	1015	1022	
A_1 CH_3 deform	1371(1370)	1309	1312	1374	1323	1334	1383
	1413(1397)	1334	1340	1402	1351	1367	
E CH_3 deform	1483(1477)	1408	1412	1471	1417	1441	1482
	1516(1508)	1434	1445	1503	1450	1478	
A_1 C−H str	3110(3104)	3037	3030	3112	3052	3066	3074
	3162(3112)	3029	3025	3106	3044	3060	
E C−H str	3229(3223)	3160	3145	3226	3170	3179	3166
	3242(3225)	3137	3126	3210	3147	3162	
			Cl^----CH_3I				
E Cl^- bend	70(65)	55	57	65	62	73	
	66(58)	48	50	65	58	72	
A_1 Cl−C str	103(100)	65	71	97	82	99	
	101(98)	58	65	95	77	93	
A_1 C−I str	473(474)	424	386	439	396	360	
	505(505)	449	414	465	424	393	
E CH_3 rock	881(875)	817	818	872	822	836	
	895(884)	824	829	884	834	857	
A_1 CH_3 deform	1218(1222)	1157	1153	1216	1153	1169	
	1263(1244)	1179	1190	1243	1192	1206	
E CH_3 deform	1444(1435)	1370	1378	1430	1379	1400	
	1471(1467)	1401	1416	1466	1417	1443	
A_1 C−H str	3149(3142)	3089	3084	3161	3105	3115	
	3201(3150)	3084	3080	3157	3100	3111	
E C−H str	3290(3281)	3241	3232	3304	3257	3257	
	3301(3282)	3219	3210	3286	3236	3238	
			$[Cl$--CH_3--$I]^-$				
E Cl−C−I bend	178(175)	164	153	167	152	159	
	187(184)	170	158	162	157	165	
A_1 Cl−C−I str	171(170)	150	139	160	138	154	
	179(179)	155	143	173	141	156	
E CH_3 rock	921(914)	841	812	881	811	845	
	951(948)	864	834	903	832	865	
A_2 out-of-plane bend	1023(986)	903	910	1012	916	954	
	983(987)	912	916	1016	921	962	
E CH_3 deform	1440(1404)	1330	1346	1396	1348	1371	
	1427(1424)	1349	1371	1419	1373	1400	
A_1 C−H str	3216(3206)	3141	3143	3224	3164	3173	
	3266(3217)	3143	3144	3225	3163	3176	
E C−H str	3426(3419)	3360	3355	3437	3379	3381	
	3441(3421)	3345	3342	3427	3364	3371	
reaction coordinate	437*i*(450*i*)	317*i*	292*i*	367*i*	293*i*	309*i*	
	489*i*(481*i*)	330*i*	307*i*	388*i*	315*i*	329*i*	
			$ClCH_3$---I^-				
E I^- bend	74(71)	42	45	62	53	63	
	60(59)	37	36	62	44	50	
A_1 C−I str	74(74)	46	49	64	87	70	
	74(73)	41	41	63	51	66	
A_1 Cl−C str	677(674)	688	631	679	637	624	
	701(690)	696	641	688	646	631	
E CH_3 rock	1003(999)	965	959	1003	982	968	
	1021(1010)	977	975	1024	981	984	
A_1 CH_3 deform	1318(1320)	1289	1289	1334	1294	1289	
	1361(1344)	1312	1318	1363	1319	1316	
E CH_3 deform	1465(1458)	1401	1404	1455	1406	1424	
	1490(1484)	1427	1438	1489	1439	1462	
A_1 C−H str	3139(3133)	3066	3060	3142	3080	3098	
	3187(3139)	3057	3054	3136	3072	3091	
E C−H str	3272(3264)	3200	3190	3269	3210	3227	
	3282(3265)	3175	3167	3250	3188	3206	

[a] Frequencies are in units of cm^{-1}. [b] Upper values are calculated with the ECP/d basis set. [c] Lower values are calculated with the ECP/t basis set. [d] Values in parentheses are calculated with MP2 theory and the frozen core orbital method (fc). [e] The experimental harmonic frequencies of CH_3I and CH_3Cl are from ref 88.

TABLE 3: Electronic Structure Theory Energies for $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ Stationary Points[a]

	stationary points			
theory	Cl^----CH_3I	$[Cl$--CH_3--$I]^-$	I^----CH_3Cl	$I^- + CH_3Cl$
MP2/ECP/6-31+G(d)	−10.7 (−10.7)[b]	−4.6 (−4.6)	−28.6 (−28.5)	−20.9 (−20.8)
MP2	−12.1 (−11.6)[c]	−4.9 (−4.0)	−22.4 (−21.6)	−13.0 (−12.2)
	−11.5 (−11.2)[d]	−2.6 (−2.1)	−20.5 (−19.2)	−10.5 (−9.2)
OPBE	−8.8	−4.8	−20.1	−14.3
	−8.1	−3.6	−19.0	−13.3
OLYP	−9.2	−5.5	−18.9	−12.6
	−8.5	−4.0	−17.6	−11.5
BhandH	−11.3	−6.4	−24.6	−16.3
	−10.8	−4.7	−23.7	−15.8
HCTH407	−11.4	−7.6	−21.7	−13.8
	−10.7	−5.8	−20.1	−12.3
B97-1	−11.5	−8.5	−21.6	−12.8
	−11.0	−7.0	−20.6	−12.2
CCSD(T)/CBS	−11.5	−5.4	−24.0	−15.5
	[−11.4][e]	[−5.2]	[−23.1]	[−14.7]

[a] Energies (kcal/mol) are with respect to the $Cl^- + CH_3I$ reactants and do not include zero-point energy (ZPE). [b] Values in parentheses are calculated with MP2 theory and the frozen core (fc) orbital method. [c] Upper values are calculated with the ECP/d basis set. [d] Lower values are calculated with the ECP/t basis set. [e] Values in square brackets include ZPE, with ZPE calculated at the MP2/PP/d level of theory (see the text). The frozen core (fc) orbital method was used for the CCSD(T) calculations.

TABLE 4: CCSD(T)/CBS Energies for $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ Stationary Points and Comparison with Experimental and Previous Theoretical Values[a]

	stationary point			
theory	Cl^----CH_3I	$[Cl$--CH_3--$I]^-$	I^----CH_3Cl	$I^- + CH_3Cl$
CCSD(T)/PP/d[b]	−11.7	−5.8	−21.4	−12.2
CCSD(T)/PP/t	−11.4	−4.9	−22.1	−13.3
CCSD(T)/PP/q	−11.5	−5.2	−23.2	−14.6
CCSD(T)/PP/5	−11.5	−5.3	−23.7	−15.2
CCSD(T)/CBS	−11.5	−5.4	−24.0	−15.5
	[−11.4]	[−5.2]	[−23.1]	[−14.7]
G2(+)[c]		−3.4		
	[−10.9]	[−3.3]	[−20.2]	[−11.9]
MP2/PTZ+[d]		−2.7		−13.5
		[−2.7]		[−12.7]
expt		−2.7[e]		−14.5[g]
		[−4.6][f]		[−13.7][g]

[a] Energies (kcal/mol) are with respect to the reactants $Cl^- + CH_3I$ and do not include zero-point energy (ZPE). The values in square brackets include ZPE, with ZPE calculated at the MP2/PP/d level of theory (see the text). The frozen core (fc) orbital method was used for the CCSD(T) calculations. [b] For the PP/x basis sets, x = d, t, q, and 5, the aug-cc-pVXZ (X = D, T, Q, and 5) basis set was used for the C, H, and Cl atoms and the aug-cc-pVXZ basis with a pseudopotential (PP) was used for iodine. [c] From ref 54. [d] From ref 83. [e] Classical barrier height obtained by fitting the experimental rate constant with TST; from ref 83. [f] The 0 K barrier, with ZPE included, obtained by fitting the reaction rate constant with an ion−molecule capture statistical model; from ref 25. [g] The reaction exothermicity at 0 K without ZPE calculated from standard molar enthalpies of formation in ref 90 and harmonic frequency data in ref 88. The values in square brackets include ZPE.

$ClCH_3$---I^- with DFT/OLYP theory, and smallest and 0.024 Å for the Cl--C bond of $[Cl$--CH_3--$I]^-$ with DFT/BhandH theory.

DFT gives significantly longer Cl^----C and C---I^- bonds for the complexes, and longer Cl--C and C--I bonds for the TS, than does MP2. For the Cl^----CH_3I and $ClCH_3$---I^- complexes, the hybrid functionals (B97-1 and BhandH) appear to give better geometries than the GGA functionals (OPBE, OLYP, HCTH), when compared with MP2 geometries. The largest difference in the geometries given by MP2 theory and the different functionals of DFT is for the C---I^- bond length of the $ClCH_3$---I^- postreaction complex. The DFT functionals give larger values for this bond length and, using the ECP/d basis set, the smallest and largest differences with MP2 are 0.078 and 0.482 Å for the B97-1 and OPBE functionals, respectively. For the ECP/t basis, the B97-1 and OPBE functionals still give the smallest and largest differences with MP2, which are 0.140 and 0.571 Å, respectively.

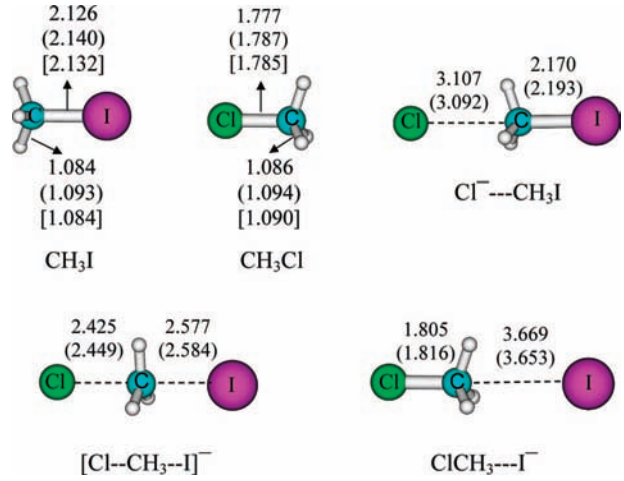

Figure 2. Geometries of stationary points for the $Cl^- + CH_3I \rightarrow ClCH_3 + I^-$ reaction optimized at the BhandH level of theory, and comparison with experiment.[87] Bond lengths are in Å. The ECP/t values are not enclosed in parentheses and brackets. The ECP/d and experimental values are enclosed in parentheses and brackets, respectively.

As shown in Table 1, the accuracy of the structures calculated for the CH_3I reactant and CH_3Cl product, in comparison with experiment,[87] depends on the level of theory and basis set. Of the methods considered here, BhandH with either the ECP/d or ECP/t basis set gives the best agreement with the experimental structures when considering both CH_3I and CH_3Cl. The BhandH structures, and their comparison with experiment, are summarized in Figure 2.

It is of interest to consider some of the specific differences of the CH_3I and CH_3Cl structures calculated by different basis sets. As discussed above, the ECP/t basis gives shorter C−H, C−I, and C−Cl bond lengths. The ECP/d and ECP/t basis sets give values for the C−H bond length of CH_3I whose difference ranges from 0.015 Å for MP2 to 0.006 Å for DFT/OPBE. The difference in the ECP/d and ECP/t values for the C−H bond length of CH_3Cl ranges from 0.014 Å for MP2 to 0.005 Å for

DFT/OPBE. The differences in the ECP/d and ECP/t bond lengths are even larger for the C−I and C−Cl bond lengths of CH_3I and CH_3Cl. For the C−I bond, the difference in the ECP/d and ECP/t bond lengths varies from 0.028 Å for MP2 to 0.014 Å for BhandH and B97-1. For the C−Cl bond length, this difference varies from 0.020 Å for MP2 to 0.006 Å for OLYP. When used with MP2 theory, the ECP/d and ECP/t basis sets give larger differences in the C−H, C−I, and C−Cl bond lengths than when used with the different DFT functionals. The bond angles of CH_3I and CH_3Cl are less sensitive to the basis set than are the bond lengths.

The geometries of the pre- and postreaction complexes and transition state have been previously calculated at the G2(+) level.[54] The structures obtained by our calculations are consistent with those determined from the G2(+) level with bond angle differences 1.1° or less. The major structural difference lies in the C---I^- bond length of the postreaction $ClCH_3$---I^- complex. The G2(+) value for this bond length is 3.741 Å. The BhandH method gives a C---I^- bond length closest to the G2(+) value, and only 0.072 Å and 0.088 Å shorter with the ECP/t and ECP/d basis sets, respectively. The difference with G2(+) theory, for the C---I^- bond length, is largest for the OPBE functional.

The geometry of the transition state was calculated previously with MP2/PTZ+ theory.[83] The structural difference between our calculations and MP2/PTZ+ mainly lies in the Cl--C bond length. The MP2/PTZ+ value is 2.350 Å, with which MP2/ECP/t gives the best agreement and only differs by 0.024 Å. HCTH407 theory gives the largest difference, with the MP2/PTZ+ TS Cl--C bond length, for both the ECP/d and ECP/t basis sets.

B. Vibrational Frequencies. Vibrational frequencies were calculated for all the stationary points by using the MP2 and DFT theories with both the ECP/d and ECP/t basis sets, and the results are listed in Table 2. These calculations were used to compare MP2 and DFT frequencies, and to compare them with experiments and other theoretical calculations. The frequencies calculated at the MP2 and MP2(fc) theories are quite consistent with the largest difference of 37 cm^{-1} (out-of-plane bend of $[Cl--CH_3--I]^-$) with the ECP/d basis and 51 cm^{-1} (A_1 C−H stretch of Cl^----CH_3I) with the ECP/t basis. The calculated frequencies of the CH_3I reactant and CH_3Cl product at the different levels of theory agree very well with experiment.[88] For the ECP/d basis, the average deviation is 1%, 2%, 3%, 1%, 2%, and 2% at the MP2, OPBE, OLYP, BhandH, HCTH407, and B97-1 theories, respectively. For the ECP/t basis the average deviation is 3%, 1%, 2%, 2%, 1%, and 1%, respectively.

The ECP/d and ECP/t basis sets give similar vibrational frequencies, with a largest difference of 54 cm^{-1} (A_1 C−H stretch of CH_3I) for MP2, 31 cm^{-1} (E CH_3 deform of Cl^----CH_3I) for OPBE, 35 cm^{-1} (E CH_3 deform of CH_3I) for OLYP, 56 cm^{-1} (A_1 C−H stretch of CH_3I) for BhandH, 39 cm^{-1} (A_1 CH_3 deform of Cl^----CH_3I) for HCTH407, and 43 cm^{-1} (E CH_3 deform of Cl^----CH_3I) for B97-1, respectively. In general, the MP2 and DFT frequencies are in quite good agreement. However, a notable exception is the larger MP2 value for the imaginary reaction coordinate frequency as compared to the DFT functional values. With the ECP/t basis set the relative MP2:BhandH:OPBE:B97-1:HCTH407:OLYP values for this imaginary frequency are 1.59:1.26:1.07:1.07:1.03:1.00 and with the ECP/d basis set the relative values are 1.50:1.26:1.09:1.06:1.00:1.00. That the MP2 value for this frequency is substantially larger than the DFT values illustrates that the MP2 and DFT theories have different potential energy surface shapes in the vicinity of the $[Cl--CH_3--I]^-$ central barrier.

There are several interesting effects concerning the frequencies calculated for CH_3I and CH_3Cl with the ECP/d and ECP/t basis sets and the MP2 and DFT theories. For the C−I and C−Cl stretches the ECP/t basis gives higher frequencies when used with both MP2 and DFT, consistent with the shorter bond lengths found with ECP/t as compared to ECP/d. Higher C−H stretch frequencies with ECP/t are also found for MP2, but not for DFT. Though the C−H bond distances are shorter when using ECP/t instead of ECP/d, for both MP2 and DFT, for DFT the ECP/t *E*-symmetry C−H stretch frequencies are significantly smaller than the ECP/d values. This same opposite trend for DFT, as compared to MP2 when using the ECP/d and ECP/t basis sets, is seen for the *E*-symmetry C−H stretch frequencies of the complexes and the central barrier.

Frequencies for CH_3I, CH_3Cl, and the transition state $[Cl--CH_3--I]^-$ have been calculated at the MP2/PTZ+ level.[83] The largest difference between the frequencies of MP2/ECP/t and those of MP2/PTZ+ is for the A_1 C−H stretch of CH_3I, for which the MP2/ECP/t value is 49 cm^{-1} larger. The principal difference between the frequencies of the DFT/ECP/t methods and those given by MP2/PTZ+ lies in the central barrier's imaginary frequency, and similar to the difference discussed above between MP2 and the DFT methods. The MP2/PTZ+ value for this frequency is 474*i* cm^{-1}. The ratio of this frequency divided by a DFT value ranges from 1.22 (BhandH) to 1.54 (OLYP). Since the two theories are fundamentally the same, MP2/ECP/t gives the best agreement with the MP2/PTZ+ calculations.

C. Energies. ***1. MP2 and DFT Energies.*** MP2 and DFT electronic structure energies, for stationary points on the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ PES, are listed in Table 3. Though MP2 with the ECP/6-31+G(d) basis set method gives energies for Cl^----CH_3I and $[Cl--CH_3--I]^-$ similar to those obtained with the larger basis sets, this smaller basis set gives energies for $ClCH_3$---I^- and $CH_3Cl + I^-$ much lower than those determined with the larger basis sets and is not considered further. There are differences in the MP2 energies calculated with and without the frozen core (fc) approximation. For the ECP/d basis these differences range from 0.3 to 0.9 kcal/mol and from 0.1 to 1.3 kcal/mol for the ECP/t basis. For both the MP2 and DFT calculations, the stationary point energies with the ECP/t basis are higher than those with the ECP/d basis. The size of this difference depends on the stationary point, and it ranges from 0.5−0.7, 1.2−2.3, 0.9−1.9, and 0.6−2.5 kcal/mol for Cl^----CH_3I, $[Cl--CH_3--I]^-$, $ClCH_3$---I^-, and $CH_3Cl + I^-$, respectively. The differences between the ECP/d and ECP/t energies are most pronounced for MP2.

The different theories and ECP/d and ECP/t basis sets give quite a range of energies for each stationary point, which are 4.0, 5.9, 7.0, and 5.8 kcal/mol for Cl^----CH_3I, $[Cl--CH_3--I]^-$, $ClCH_3$---I^-, and $CH_3Cl + I^-$, respectively. A reference for the stationary point energies was determined by performing high-level CCSD(T) calculations, as discussed in the next section.

2. CCSD(T) Energies. CCSD(T) calculations, based on the MP2/PP/d optimized geometries, were performed with the PP/d, PP/t, PP/q, and PP/5 basis sets and the resulting energies are listed in Table 4. These energies were extrapolated to the complete basis set (CBS) limit by using the formula proposed by Peterson et al.[85]

$$E(n) = E_{CBS} + A \exp[-(n-1)] + B_{exp}[-(n-1)^2] \quad (2)$$

where $n = 2$, 3, 4, and 5 representing the PP/d, PP/t, PP/q, and PP/5 basis sets. The CBS energies are also included in Table 4. The CCSD(T)/CBS energies for Cl^----CH_3I, $[Cl--CH_3--I]^-$,

$ClCH_3$---I^-, and products are ~0, 0.1, 0.3, and 0.3 kcal/mol lower than the CCSD(T)/PP/5 values, respectively, which shows good convergence toward the complete basis set limit for the CCSD(T) energies.

The resulting CCSD(T)/CBS energies are given in Figure 1 and listed in Table 3 where they are compared with the MP2 and DFT energies. The BhandH/ECP/t energies are in the best agreement with the CCSD(T)/CBS energies. The largest difference between these two sets of energies is 0.7 kcal/mol for the Cl^----CH_3I complex and TS. For MP2, MP2/ECP/d gives the best agreement with the CCSD(T)/CBS energies with the largest difference of 2.5 kcal/mol for the products. The central barrier height calculated at OLYP/ECP/d theory is in the best agreement with the CCSD(T)/CBS value, with a small difference of 0.1 kcal/mol.

The role of ZPE on the stationary point energies is illustrated for the CCSD(T)/CBS calculations. The effect is small for Cl^----CH_3I and $[Cl\text{--}CH_3\text{--}I]^-$, but almost 1 kcal/mol for $ClCH_3$---I^- and $CH_3Cl + I^-$, where the effect of including ZPE increases the stationary point energy. This latter effect results from the higher vibrational frequencies for the product CH_3Cl, as compared to the reactant CH_3I.

3. Comparison with Experimental and Previous Theoretical Energies. Energies for the stationary points have been determined from G2(+)[54] and MP2/PTZ+[83] ab initio calculations in previous studies. They are listed in Table 4, where they are compared with the CCSD(T) energies. With respect to the $Cl^- + CH_3I$ reactants, G2(+) gives energies (zero-point energies are included) of −10.9, −3.3, −20.2, and −11.9 kcal/mol for Cl^----CH_3I, $[Cl\text{--}CH_3\text{--}I]^-$, $ClCH_3$---I^-, and $CH_3Cl + I^-$, respectively. For CCSD(T)/CBS these energies are −11.4, −5.2, −23.1, and −14.7 kcal/mol. The largest difference between CCSD(T)/CBS and G2(+) energies is 2.9 kcal/mol for the $ClCH_3$---I^- complex. At the MP2(fc)/ECP/d level of theory, these energies are −11.4, −3.9, −20.6, and −11.4 kcal/mol, and are in quite good agreement with the G2(+) energies, but are 1.3, 2.5, 3.3 kcal/mol more positive for the central barrier, $ClCH_3$---I^- complex, and products as compared to CCSD(T)/CBS. Similarly, the MP2/PTZ+ energies agree with the G2(+) values, but are more positive for the central barrier and products than the CCSD(T)/CBS values.

The complexation energies calculated here at the highest level of theory, i.e. CCSD(T)/CBS, are in agreement with those found from accurate HPMS experiments.[89] The classical complexation energies calculated for Cl^----CH_3I and I^----CH_3Cl are −11.5 and −8.5 kcal/mol. As shown in Table 4, including ZPE has only a small effect on these energies (i.e., 0.1 kcal/mol) and a small effect is also expected if a 298 thermal energy is included.[53,54] Complexation energies of X^----CH_3Y complexes depend primarily on the identity of X^- and to a much smaller extent on the identity of CH_3Y.[54] Thus, the experimental complexation enthalpies, $\Delta H_{comp}(298)$ for Cl^----CH_3Y complexes, lie in a fairly narrow range.[54,89] The experimental $\Delta H_{comp}(298)$ is −10.4 and −12.5 kcal/mol for Cl^----CH_3I and Cl^----CH_3Br, respectively. To convert these enthalpies to energies at 298 K, 0.6 kcal/mol is added, giving energies slightly less negative. The above CCSD(T)/CBS complexation energy for Cl^----CH_3I is −11.5 kcal/mol and quite consistent with the above experimental complexation energies. Though an experimental complexation enthalpy has not been reported for I^----CH_3Cl an accurate HPMS value of $\Delta H_{comp}(298) = -9.3$ kcal/mol has been reported for I^----CH_3I, which is ~1 kcal/mol more negative than the CCSD(T)/CBS classical complication energy for I^----CH_3Cl.

The experimental reaction exothermicity of −14.5 kcal/mol,[90] listed in Table 4, is 1 kcal/mol more positive than the CCSD(T)/CBS value. The OPBE/ECP/d (Table 3) exothermicity is in the best agreement with the experimental exothermicity with a difference of 0.2 kcal/mol. The BhandH functional gives stationary point structures in good agreement with experiment and has a reaction exothermicity only 1.8 (ECP/d) and 1.3 (ECP/t) kcal/mol different than the experimental value (see Table 3).

Values of −2.7 and −4.6 kcal/mol for the $[Cl\text{--}CH_3\text{--}I]^-$ central barrier height have been estimated by fitting the 300 K experimental rate constant using TST[83] and an ion−molecule capture statistical model.[25] However, the accuracy of these fits is somewhat uncertain given that experiments,[23−31] chemical dynamics simulations,[32−50] and quite-detailed statistical rate theory calculations[91,92] suggest that TST and statistical theories are not accurate models for S_N2 reaction kinetics. However, it is worthwhile noting that, even if these models give rate constants in error by a factor of 10, this translates into only a 1.4 kcal/mol error in the barrier height! The expected effect of the TST and statistical model is to overestimate the $Cl^- + CH_3I$ rate constant and, if this overestimation is a factor of 10, the actual barrier is then 1.4 kcal/mol lower than that deduced from the modeling. This would lower the estimated experimental central barrier heights to −4.1 and −6.0 kcal/mol, values quite consistent with the CCSD(T)/CBS barrier (Table 4). Thus, because of the above uncertainties in fitting the experimental rate constant it is difficult to deduce an accurate "experimental" central barrier height. A survey of all the electronic structure theory barrier heights, in Tables 3 and 4, indicates that the DFT/B97-1 central barrier may be too low.

IV. Summary

Extensive electronic structure calculations were performed for stationary points on the potential energy surface for the $Cl^- + CH_3I \rightarrow ClCH_3 + I^-$ S_N2 nucleophilic substitution reaction to compare with experiment and to compare different electronic structure theories. The calculations were performed with the MP2 and CCSD(T) theories and the DFT functionals OPBE, OLYP, HCTH407, BhandH, and B97-1. For the MP2 and DFT calculations, the aug-cc-pVDZ and aug-cc-pVTZ basis sets[82] were used for the C, H, and Cl atoms and an effective core potential (ECP)[80] for the iodine atom. These basis sets are denoted as ECP/d and ECP/t, respectively. Single point energy calculations were performed at the CCSD(T) level of theory. The complete basis set (CBS) limit was extrapolated for the CCSD(T) calculations by using the aug-cc-pVXZ (X = D, T, Q, and 5) basis sets[82] for the C, H, and Cl atoms and a pseudopotential (PP)[86] for the iodine atom. These basis sets are identified as PP/x, x = d, t, q, and 5. In the following, the results obtained for the stationary point structures, vibrational frequencies, and energies are summarized. The MP2 calculations were performed with and without the frozen core (fc) approximation. The use of this approximation has only minor effects on the structures and frequencies, but alters the relative stationary point energies by as much as 1.3 kcal/mol. Differences between the MP2/ECP/d and MP2/PP/d stationary point geometries are quite small.

A. Geometries. Though the geometries obtained with the ECP/d and ECP/t basis sets are in good agreement for all the theories, ECP/t gives shorter bond lengths than ECP/d, except for the Cl^----C and C---I^- bonds of the complexes. For these bonds, the DFT functionals give shorter bonds with ECP/d. DFT gives significantly longer halide ion/carbon atom bond lengths for the complexes than does MP2 theory. The geometries

obtained by BhandH/ECP/t theory give the best agreement with those determined with G2(+) thoery[54] and the geometries obtained by MP2/ECP/t agree best with those from MP2/PTZ+ theory.[83] BhandH, with either the ECP/d or ECP/t basis set, gives the most accurate structures in comparison with experiment[87] when considering both CH_3I and CH_3Cl.

B. Frequencies. The frequencies calculated with ECP/d and ECP/t basis sets are in good agreement with differences less than 56 cm^{-1}. The major difference between the MP2 and DFT frequencies is for the imaginary frequency of the central barrier. By using the ECP/t basis the MP2 value for this frequency is 1.59 and 1.26 times larger than those given by the OLYP and BhandH functionals, respectively. Thus, the MP2 and DFT theories have different PES shapes in the vicinity of the $[Cl^{-}\text{--}CH_3\text{--}I]^-$ central barrier. The frequencies of CH_3I and CH_3Cl, obtained at the different levels of theory and basis sets, are in excellent agreement with experiment[88] with differences ranging from 1% to 3%. For both MP2 and the DFT functionals, ECP/t gives shorter bond lengths for CH_3I and CH_3Cl than does ECP/d, and the trend is for ECP/t to give higher vibrational frequencies. The exception is for the DFT *E*-symmetry C−H stretch frequencies, which are lower for ECP/t as compared to ECP/d, even though the former gives shorter C−H bond lengths. In comparison with previous studies, the MP2/ECP/t frequencies are in the best agreement with those determined with MP2/PTZ+.[83]

C. Energies. Overall the energies obtained with the ECP/t basis set are slightly higher than those obtained with the ECP/d basis set for all the theories. CCSD(T)/CBS calculations were performed to determine approximate "benchmark" values for the stationary point energies, and the CCSD(T)/CBS results are in good agreement with experiments for the complexation energies[89] and reaction exothermicity.[90] For the latter energy, CCSD(T)/CBS is within 1 kcal/mol of experiment. The CCSD(T)/CBS value for the $[Cl\text{--}CH_3\text{--}I]^-$ central barrier height is less than the value found by fitting the experimental $Cl^- + CH_3I \rightarrow ClCH_3 + I^-$ rate constant with statistical theory,[25,83] which is consistent with the nonstatistical capture,[44,93,94] RRKM,[33,39,93] and barrier recrossing[35,37,42] dynamics[3] expected for this reaction. The BhandH energies are in overall best agreement with the CCSD(T)/CBS values, with a largest difference of only 0.7 kcal/mol for the ECP/t basis set. For MP2 theory the best agreement with the CCSD(T)/CBS energies is given by the MP2/ECP/d with the largest difference of 2.5 kcal/mol and for the products.

In summary, the work presented here has investigated the ability of different electronic structure theory methods to determine accurate stationary point properties for the $Cl^- + CH_3I \rightarrow ClCH_3 + I^-$ PES. The results illustrate the ability of the higher level CCSD(T)/CBS theory to recover the experimental complexation enthalpies and reaction exothermicity. The more approximate MP2 theory and DFT functionals, which are practical for direct dynamics simulations[51,95,96] of the $Cl^- + CH_3I$ S_N2 reaction, give different representations of its PES. At a high collision energy of 1.9 eV these methods give similar reaction dynamics, as has been reported,[31] but they give significantly different dynamics at lower collision energies.[97] The calculations reported here suggest that BhandH is the preferred method for direct dynamics simulations, since it gives reaction energies in the best agreement with the CCSD(T)/CBS values. The maximum difference is only 1.0 and 0.7 kcal/mol for the ECP/d and ECP/t basis sets, respectively. By using the ECP/d and ECP/t basis sets, a DFT direct dynamics calculation is 3 and 4 times faster, respectively, than one with MP2 and this, in itself, favors BhandH over MP2. The ECP/d basis set was used for the direct dynamics simulation reported in ref 31, but use of the ECP/t basis set is also practical, since it only requires 5 and 7 times more computer time for BhandH and MP2 direct dynamics, respectively. It will be of interest to determine whether BhandH or another electronic structure theoretical method provides an accurate representation of the low collision energy dynamics for the $Cl^- + CH_3I \rightarrow ClCH_3 + I^-$ reaction.

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