QM/MM Calculations for the Cl^- + CH_3Cl S_N2 Reaction in Water Using CM5 Charges and Density Functional Theory

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Table S1. Optimized gas-phase C-Cl distances (Å) of the isolated species, complex and TS. S2

Table S2. Optimized gas-phase charges (*e*) of the isolated species, complex and TS. S3

Figure S1. Comparison of calculated *pmfs* at different levels of QM theory. S4

Table S1. Optimized Gas Phase C-Cl distances **(Å)** of the isolated species, complex and TSs.

	$Cl^- + CH_3Cl$		Complex		TS	
Method	**Cl_1-C**	**C-Cl_2**	**Cl_1-C**	**C-Cl_2**	**Cl_1-C**	**C-Cl_2**
HF/6-31G(d)	∞	1.785	3.265	1.828	2.383	2.383
MP2/6-31G(d)	∞	1.779	3.161	1.814	2.309	2.309
MP2/6-31G+(d)	∞	1.780	3.271	1.810	2.317	2.317
MP2/6-31++G(d,p)	∞	1.778	3.255	1.807	2.310	2.310
MP2/*aug*-cc-PVTZ	∞	1.780	3.118	1.816	2.280	2.280
B3LYP/6-31+G(d)	∞	1.806	3.201	1.856	2.371	2.371
B3LYP/6-311G(2d,d,p)	∞	1.804	3.161	1.814	2.366	2.366
B3LYP-D3/6-31+G(d)	∞	1.808	3.145	1.863	2.383	2.383
M06-2X/6-31+G(d)	∞	1.787	3.255	1.807	2.314	2.314
CBS-QB3	∞	1.804	3.161	1.814	2.366	2.366
AM1	∞	1.741	3.201	1.856	2.154	2.154
PDDG-PM3	∞	1.760	2.953	1.784	2.246	2.246
CCSD-T/TZ2Pf+dif[a]		1.782	3.151	1.823	2.302	2.302

[a] Ref. S1.

Table S2. Optimized gas-phase partial charges (e) of the isolated species, complex and TSs.[a]

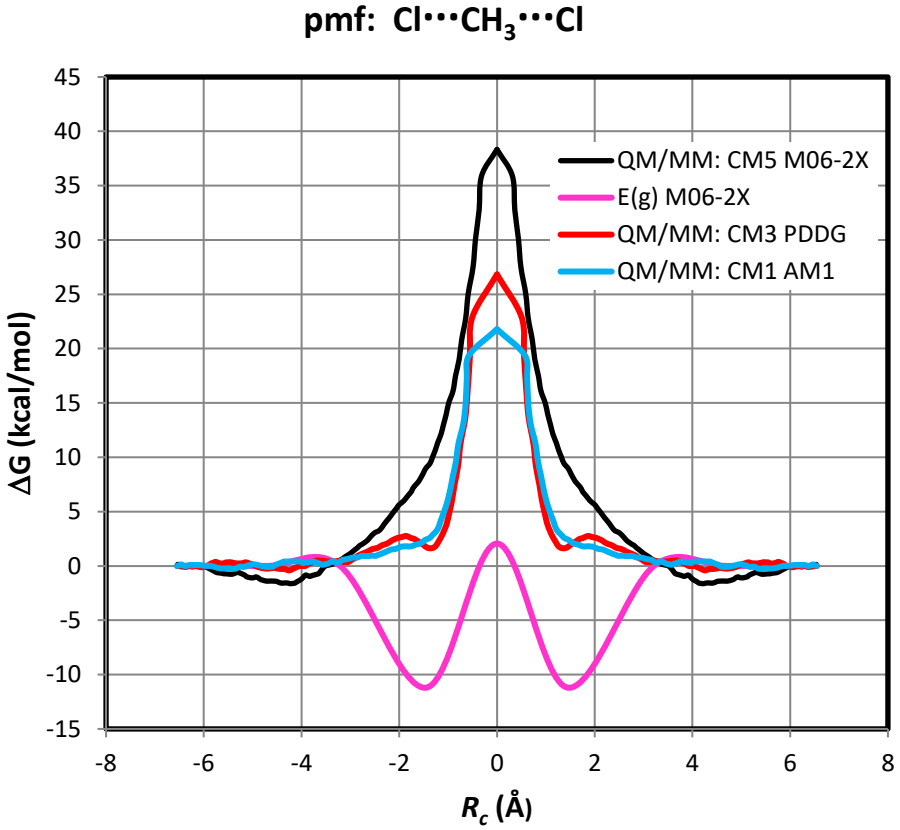
	$Cl^- + CH_3Cl$				Complex				TS			
Method	**Cl_1**	**H[b]**	**C**	**Cl_2**	**Cl_1**	**H[b]**	**C**	**Cl_2**	**Cl_1**	**H[b]**	**C**	**Cl_2**
HF/6-31G(d)	-1	0.098	-0.146	-0.147	-0.907	0.096	-0.142	-0.239	-0.679	0.117	-0.311	-0.635
MP2/6-31G(d)	-1	0.096	-0.143	-0.144	-0.894	0.092	-0.146	-0.237	-0.628	0.107	-0.064	-0.628
MP2/6-31G+(d)	-1	0.096	-0.143	-0.146	-0.893	0.090	-0.148	-0.230	-0.626	0.106	-0.064	-0.626
MP2/6-31++G(d,p)	-1	0.097	-0.147	-0.144	-0.891	0.090	-0.152	-0.227	-0.624	0.106	-0.069	-0.624
MP2/*aug*-cc-PVTZ	-1	0.097	-0.151	-0.141	-0.869	0.088	-0.157	-0.238	-0.610	0.101	-0.083	-0.610
B3LYP/6-31+G(d)	-1	0.101	-0.172	-0.132	-0.854	0.089	-0.183	-0.230	-0.568	0.096	-0.151	-0.568
B3LYP-D3/6-31+G(d)	-1	0.101	-0.171	-0.132	-0.845	0.088	-0.184	-0.235	-0.569	0.096	-0.149	-0.569
M06-2X/6-31+G(d)	-1	0.102	-0.173	-0.131	-0.859	0.089	-0.184	-0.224	-0.570	0.095	-0.145	-0.570
CBS-QB3	-1	0.097	-0.145	-0.145	-0.872	0.089	-0.145	-0.251	-0.628	0.105	-0.059	-0.628
CM1/AM1[c]	-1	0.112	-0.166	-0.170	-0.982	0.117	-0.066	-0.304	-0.734	0.106	0.151	-0.734
CM3/PDDG-PM3[c]	-1	0.128	-0.175	-0.208	-0.988	0.118	-0.145	-0.220	-0.767	0.098	0.241	-0.767

[a] CM5 charges except where noted. All calculations made with Gaussian 16.

[b] The charge of an arbitrary H is given; some are slightly different.

[c] BOSS single-point calculation on Gaussian16 geometry.

Figure S1. Comparison of Calculated *pmfs* at Different Levels of QM theory.



REFERENCES

S1. Gonzales, J. M.; Allen. W. D.; Schaefer, H. F. III Model Identity S_N2 Reactions CH_3X+X (X=F, Cl, CN, OH, SH, NH_2, PH_2): Marcus Theory Analyzed. *J. Chem. Phys. A* **2005**, *109*, 10613-10628.