Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

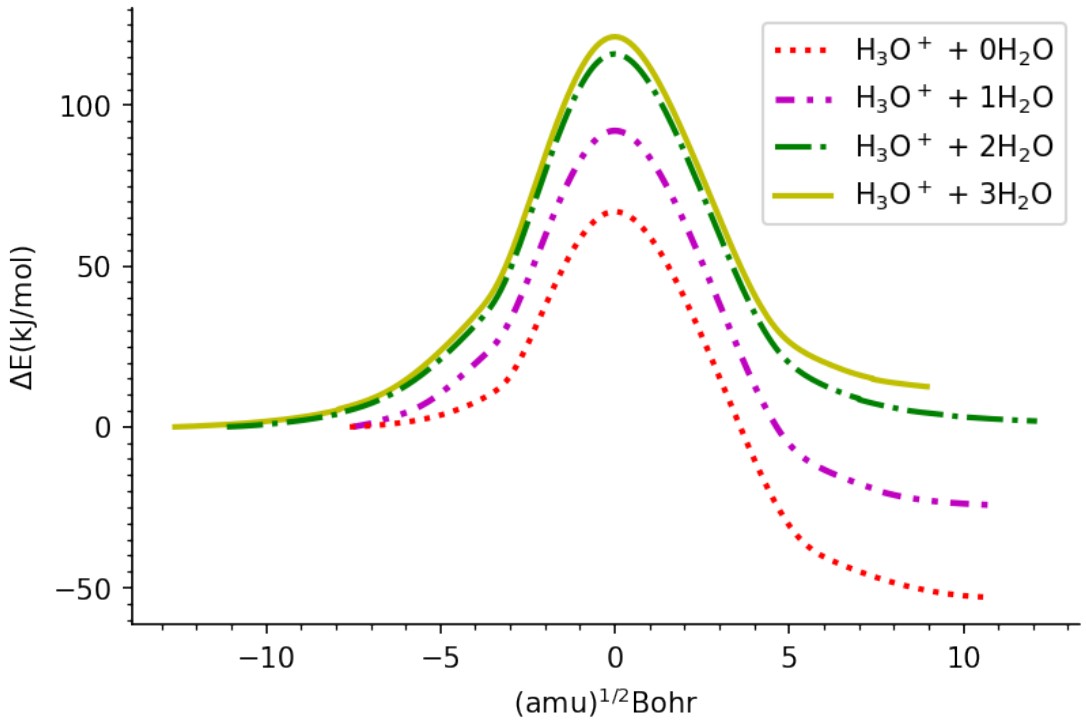


Figure S1: IRC curves for the S_N2 with zero to three explicit solvent molecules, at the M06-2X/6-31++G(d,p)/SMD(Water) level.

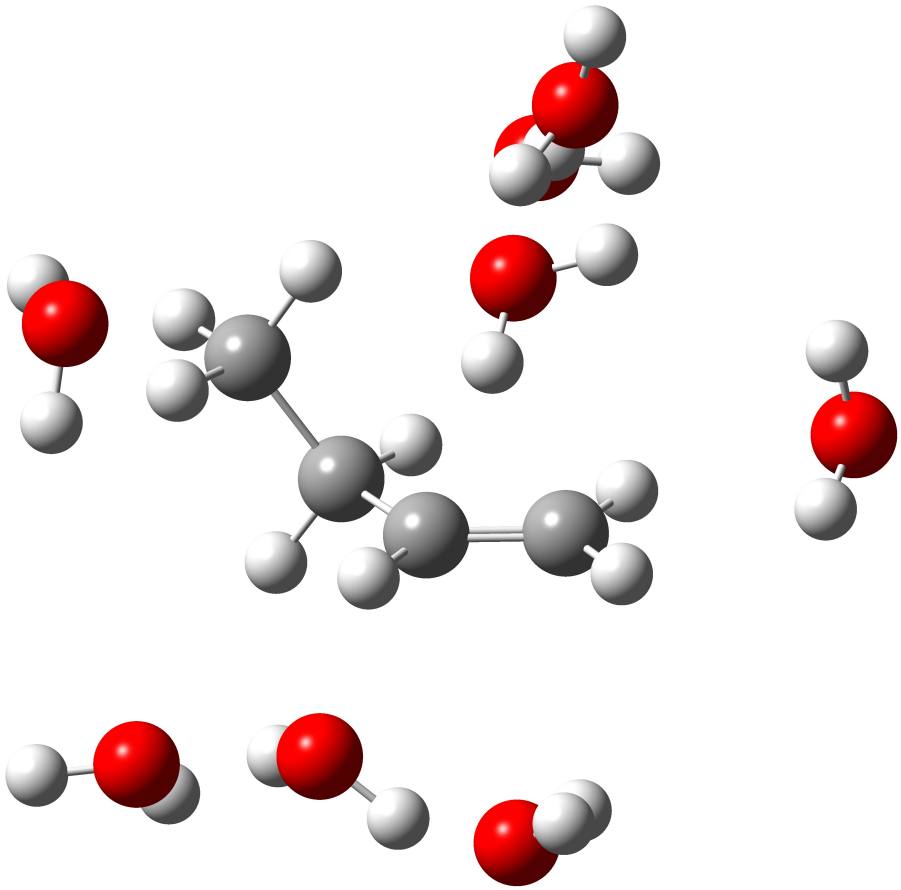
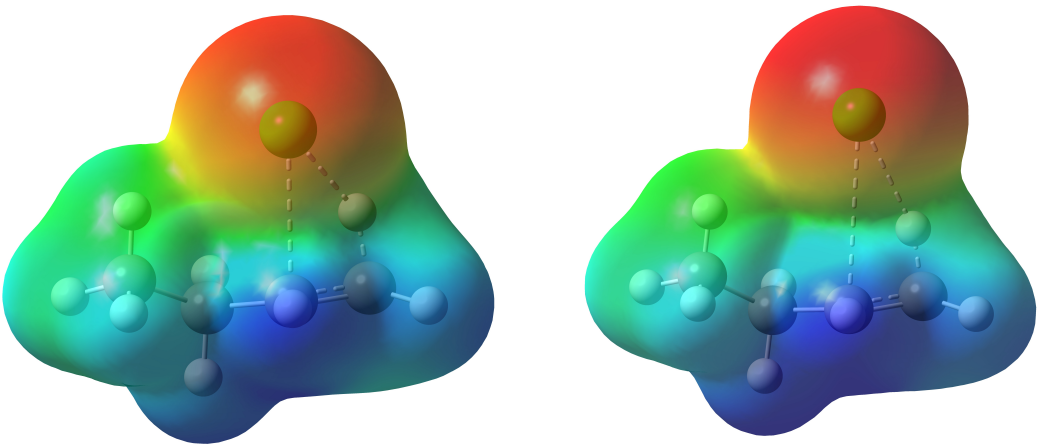


Figure S2: Extracted structure of butene with eight water molecules from the DICE3 simulation.



(a) (b)

Figure S3: Molecular electrostatic potential for the reaction of 1-butene with HCl in the gas phase and using the implicit solvation model. The surfaces were prepared using an isovalue of 0.004 for the density, and $E = \pm 0.09$ and $E = \pm 0.13$, for the gas phase and SMD respectively.

Table S1: TSs calculated with different amounts of explicitly added solvent molecules and the BSSE corrected energy variation between successive TSs. The energy variation corresponds to the next line minus the current line, plus the number of water molecules. The results were obtained at M06-2X/6-31++G(d,p)/SMD(Water) level of theory.

TS[(a)]	Energy (a.u.)	ΔE(TS$^{\#}$) (kJ.mol^{-1})
TS · 0 H_2O	-157.54006	2.76
TS · 1 H_2O	-233.94883	-17.39
TS · 2 H_2O	-310.36375	-10.00
TS · 3 H_2O	-386.77665	-14.70
TS · 4 H_2O	-463.19132	-16.28
TS · 5 H_2O	-539.60659	-16.64
TS · 6 H_2O	-616.02200	-18.49
TS · 7 H_2O	-692.43811	-18.13
TS · 8 H_2O	-768.85408	-

[(a)] TS = $H_3CH_2C^{(+)}(OH_2)H{-}CH_3$ (Carbocation). [(b)] $\Delta E(TS{\cdot}1\ H_2O) = E(TS{\cdot}2\ H_2O)$ - [$E(TS{\cdot}1\ H_2O)$ + $E(H_2O)$], where $E(H_2O)$ = -76.40907 a.u.

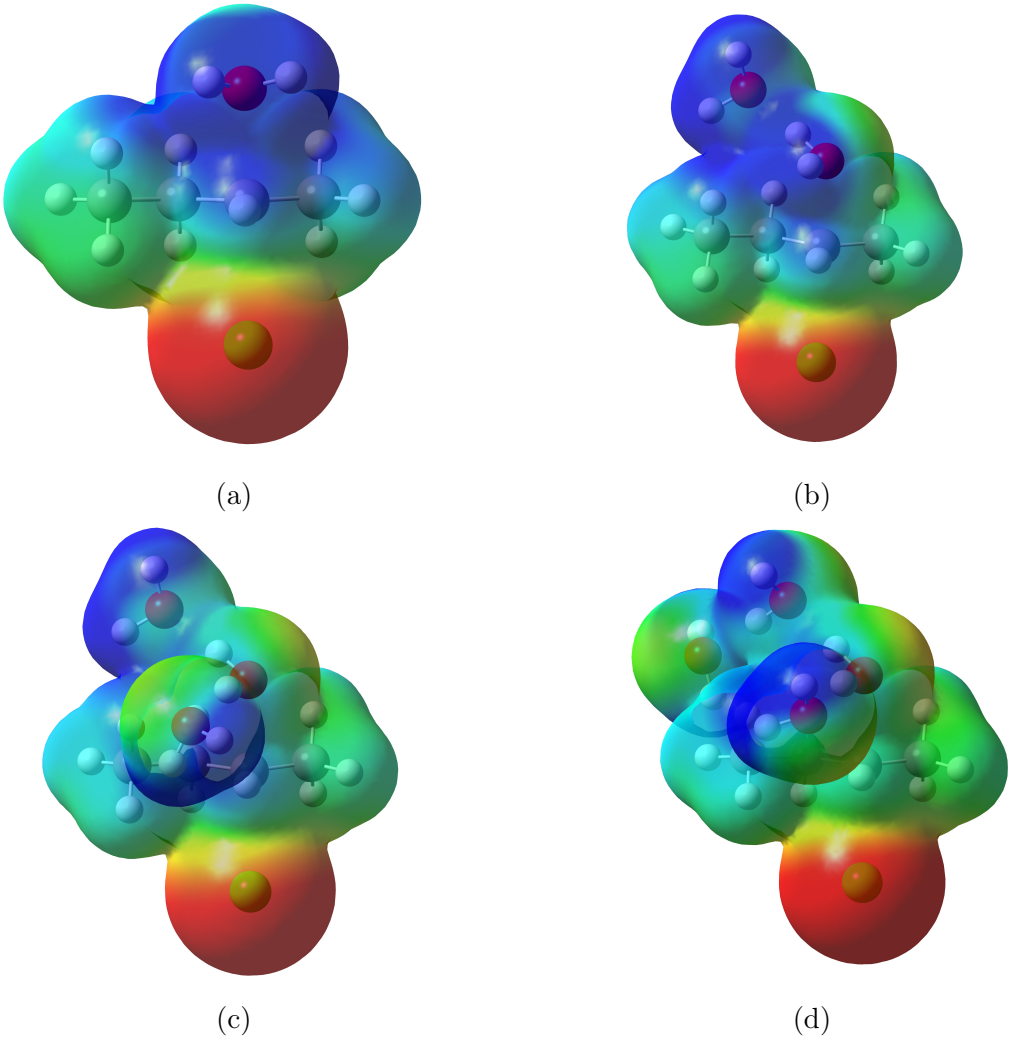
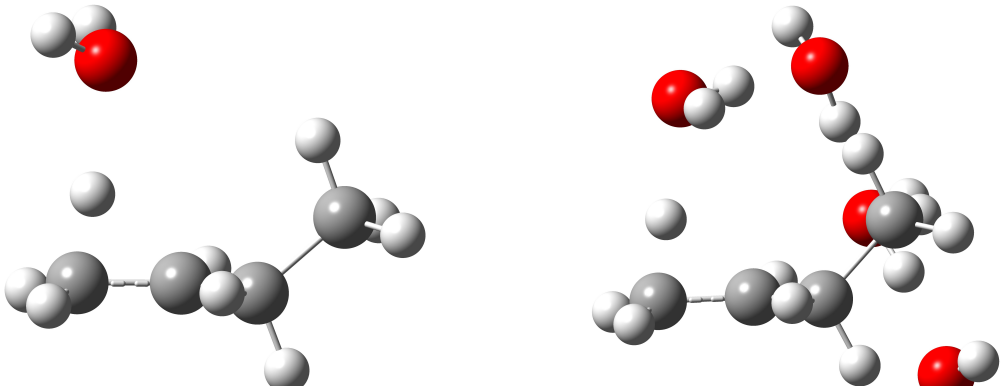


Figure S4: Molecular electrostatic potential for the S_N2 reaction TSs with (a) zero, (b) one, (c) two and (d) three explicit solvent molecules, obtained at M06-2X/6-31++G(d,p)/SMD(Water). The surfaces were prepared using an isovalue of 0.004 for the density, and $E_{min} = \pm 0.101$.



(a) (b)

Figure S5: Representations of the different dihedrals the water molecule part of the hydronium ion adopts for TS $\cdot$ nH_2O with (a) n = 0 and (b) n = 7. An inversion of the angle of hH1 and hH2 in relation to the plane of the double bond can be clearly seen.

Table S2: Bond distances, angles and dihedrals for the relevant atoms of the TS structures of the hydration reaction with 0 to 7 added explicit solvent molecules. "WAT dist" and "WAT angle" are the distances and angles for the explicitly added solvents and the first two are always interacting with hH1 and hH2, while the rest are in order of addition.

Molecule	C1-C2	C1-tH	C2-C1-tH	C1-tH-hO	hO-tH	hH1-hO	hH2-hO	tH-hO-hH1	tH-hO-hH2	tH-hO-hH1-hH2	WAT dist	WAT angle
TS · 0 H_2O	1.39194	1.19246	81.25705	174.43474	1.79656	0.96757	0.96757	107.19387	110.96811	118.06048	-	-
TS · 1 H_2O	1.39872	1.17422	83.13558	165.42531	1.88221	0.96613	0.98024	113.16253	102.40913	111.21643	1.81346	175.12754
TS · 2 H_2O	1.39945	1.17207	83.11344	164.21958	1.88040	0.97686	0.97716	118.21117	108.83495	122.97498	1.85327	174.04965
											1.83376	172.81391
TS · 3 H_2O	1.39742	1.17752	82.18465	163.54692	1.8548	0.9772	0.97922	116.74025	112.14527	126.01696	1.82039	177.7193
											1.83191	175.05152
											1.82432	176.73033
TS · 4 H_2O	1.39737	1.18317	83.19468	171.14772	1.84191	0.97955	0.97982	94.19132	99.07688	-100.84622	1.82396	169.90601
											1.81663	167.10738
											1.80705	175.16637
											1.81132	174.98704
TS · 5 H_2O	1.38718	1.2106	76.66185	164.45459	1.80134	0.97906	0.9797	101.92932	110.78176	-116.12896	1.81855	173.41491
											1.85197	174.41207
											1.80684	170.70510
											1.84139	177.47075
											1.85060	172.00419
TS · 6 H_2O	1.39328	1.2002	84.7615	173.32138	1.70643	0.98155	0.98152	96.84559	96.7202	-99.25854	1.80246	168.73601
											1.79976	170.30637
											1.81314	178.11195
											1.80338	173.42334
											1.77789	173.33584
											1.81821	173.45521
TS · 7 H_2O	1.39502	1.19117	82.86834	174.52714	1.78037	0.98065	0.9797	99.71346	93.1793	-96.45889	1.80606	162.90625
											1.80636	171.53061
											1.81370	177.07051
											1.79863	174.04576
											1.76954	171.95999
											1.80759	174.92089
											1.78441	172.46057

Table S3: Bond distances, angles and dihedrals for the relevant atoms of the TS structures for the S_N2 reaction with 0 to 3 added explicit solvent molecules. "WAT dist" and "WAT angle" are the distances and angles for the explicitly added solvents and the first two are always interacting with hH1 and hH2, while the rest are in order of addition.

Molecule	hO-C2	Cl-C2	hO-C2-H(C2)	Cl-C2-H(C2)	C3-C2-C1-Cl	C3-C2-C1-hO	hH1-hO	hH2-hO	C2-hO-hH1	C2-hO-hH2	WAT dist	WAT angle
TS · 0 H_2O	2.13963	2.66267	83.95312	73.23624	-100.94425	98.83627	0.96959	0.96971	108.29851	106.69161	-	-
TS · 1 H_2O	2.16295	2.62761	81.41325	74.01315	-101.44172	100.40323	0.98570	0.96824	108.55595	106.08392	1.76297	176.94908
TS · 2 H_2O	2.17561	2.59060	80.22848	74.75206	-101.86493	100.26192	0.98187	0.98060	108.04889	100.80429	1.80205	176.30455
											1.81362	166.44558
TS · 3 H_2O	2.17692	2.57972	79.91080	75.07836	-101.89334	100.13881	0.98454	0.98054	108.43710	101.04009	1.76754	178.73195
											1.80884	167.69602
											1.81011	176.99743

Table S4: Simulation parameters obtained for the TS structure of the reaction via H_3O^+.

atom	q	ϵ	σ
C	-0.146844	0.066	3.500
C	0.008368	0.066	3.500
C	0.394383	0.066	3.500
C	-0.428759	0.066	3.500
O	-0.834879	0.1521	3.1506
H	0.059112	0.030	2.500
H	0.101366	0.030	2.500
H	0.062394	0.030	2.500
H	0.084233	0.030	2.500
H	0.074522	0.030	2.500
H	0.104255	0.030	2.500
H	0.196490	0.030	2.500
H	0.191265	0.030	2.500
H	0.261292	0.030	2.500
H	0.439823	0.0000	0.0000
H	0.432980	0.0000	0.0000

Table S5: Optimized geometry for the TS of the reaction via the HCl in the gas-phase.

C	1.827799	-1.163083	0.099957
C	1.464478	0.252234	-0.334069
C	0.404431	0.912922	0.450122
C	-0.441943	1.911190	-0.063403
H	2.045769	-1.201162	1.171478
H	2.711811	-1.508125	-0.440406
H	0.988757	-1.830998	-0.106191
H	2.328357	0.928891	-0.186533
H	1.216383	0.309624	-1.399393
H	0.298938	0.626917	1.496063
H	-0.942172	2.570469	0.640374
H	-0.202644	2.320940	-1.042086
H	-1.213405	0.983097	-0.244453
Cl	-1.574140	-0.863484	-0.047323

Table S6: Optimized geometry for the TS of the reaction via the HCl with implicit solvent (SMD).

C	1.574688	-1.553710	0.120937
C	1.598296	-0.116886	-0.392518
C	0.898043	0.855135	0.432565
C	0.184745	1.958369	-0.068884
H	1.905014	-1.600067	1.161991
H	2.240383	-2.172879	-0.483101
H	0.560983	-1.955857	0.053913
H	2.631540	0.286592	-0.315119
H	1.315998	-0.013541	-1.444259
H	0.876724	0.677929	1.509988
H	-0.041588	2.762698	0.626803
H	0.357055	2.227918	-1.109847
H	-0.750657	1.260617	-0.071862
Cl	-2.037064	-0.490050	-0.028300

Table S7: Optimized geometry for the TS of the reaction via the H_3O^+ without explicit solvent molecules.

C	1.758160	-1.116792	0.101265
C	1.360841	0.283225	-0.371636
C	0.307420	0.901039	0.435826
C	-0.807346	1.556482	-0.079146
O	-2.031819	-1.166462	-0.061681
H	2.013981	-1.110354	1.163879
H	2.626539	-1.461008	-0.463037
H	0.939552	-1.822278	-0.057858
H	2.208116	0.974904	-0.205912
H	1.113660	0.326527	-1.435037
H	0.359992	0.757255	1.516903
H	-1.421285	2.146061	0.596348
H	-0.817749	1.806132	-1.138210
H	-1.258293	0.454399	-0.015753
H	-2.706748	-1.208532	-0.753701
H	-2.517668	-1.275133	0.767979

Table S8: Optimized geometry for the TS of the reaction via the H_3O^+ with one explicit solvent molecule added.

C	-0.154620	1.833990	0.723307
C	-0.850153	1.087146	-0.416869
C	-1.652336	-0.051412	0.020252
C	-1.667152	-1.298726	-0.612520
O	0.908910	-1.499275	0.975929
H	-0.879926	2.169985	1.468543
H	0.363166	2.708597	0.324052
H	0.578779	1.189046	1.214185
H	-1.625607	1.742657	-0.860557
H	-0.176671	0.800725	-1.229352
H	-2.202637	0.053303	0.957698
H	-2.444328	-2.004733	-0.333325
H	-1.253870	-1.362799	-1.618037
H	-0.754326	-1.511070	0.094899
H	1.458995	-0.948571	0.380105
H	1.335053	-2.366141	0.994912
O	2.345610	0.130058	-0.777099
H	3.301039	-0.004140	-0.716305
H	2.209737	1.060883	-0.552478

Table S9: Optimized geometry for the TS of the reaction via the H_3O^+ with two explicit solvent molecules added.

C	-2.135158	0.942719	0.985285
C	-2.166995	-0.051250	-0.175503
C	-1.592220	-1.358087	0.126028
C	-0.794869	-2.090308	-0.760844
O	1.131807	-0.069745	0.403930
O	3.904615	-0.489710	0.322631
O	0.229031	2.293235	-0.858271
H	-2.644194	0.533716	1.861810
H	-2.638105	1.865761	0.690344
H	-1.104149	1.179593	1.259251
H	-3.218221	-0.330557	-0.391721
H	-1.757057	0.347054	-1.107729
H	-1.721436	-1.745949	1.138624
H	-0.594292	-3.132286	-0.527710
H	-0.798618	-1.791693	-1.808033
H	0.070343	-1.463886	-0.278394
H	0.883400	0.763308	-0.042350
H	2.102584	-0.150135	0.330599
H	4.391235	0.156687	0.850973
H	-0.202188	2.846652	-0.192875
H	0.933290	2.844341	-1.224839
H	4.309237	-0.451297	-0.554063

Table S10: Optimized geometry for the TS of the reaction via the H_3O^+ with three explicit solvent molecules added.

C	-1.651727	-0.503075	1.518039
C	-1.537171	-1.087647	0.111225
C	-0.541646	-2.147025	-0.030067
C	0.277692	-2.311141	-1.150126
O	1.586130	-0.097485	0.400301
O	-0.140983	2.081647	0.078691
O	-2.826109	1.832404	-0.684234
O	4.234279	0.740726	-0.002774
H	-1.832127	-1.294215	2.250527
H	-2.483756	0.201890	1.558363
H	-0.736027	0.025425	1.793299
H	-2.467742	-1.636923	-0.137403
H	-1.410338	-0.335273	-0.673429
H	-0.368593	-2.796889	0.830117
H	0.838220	-3.236427	-1.245919
H	0.008796	-1.776711	-2.060010
H	0.962606	-1.556799	-0.559861
H	0.977229	0.657203	0.264088
H	2.488443	0.241695	0.239952
H	4.490313	1.380842	0.674672
H	0.231008	2.716802	-0.546930
H	-1.072513	1.960191	-0.197705
H	4.355706	1.203512	-0.842578
H	-3.173448	2.718598	-0.853155
H	-2.917212	1.362067	-1.524321

Table S11: Optimized geometry for the TS of the reaction via the H_3O^+ with four explicit solvent molecules added.

C	-0.284552	-0.839501	2.054976
H	0.665314	-1.220130	2.439123
H	-1.069553	-1.061902	2.780121
H	-0.209095	0.245158	1.947522
C	-0.632024	-1.490757	0.715073
H	-0.673835	-2.589878	0.847623
H	-1.604473	-1.182875	0.320349
C	0.408302	-1.363633	-0.302268
H	1.448132	-1.437848	0.026053
C	0.167692	-1.036723	-1.639379
H	0.975704	-1.163445	-2.355530
H	-0.854763	-1.114695	-2.006758
H	0.251602	0.072660	-1.236726
O	0.150551	1.738316	-0.456986
H	-0.696329	1.632554	0.024329
H	0.870998	1.561479	0.183320
O	2.375573	1.036657	1.055645
H	2.843765	0.448488	0.427621
O	-2.394441	1.361937	0.632630
H	-2.856949	2.209826	0.610006
H	-2.779290	0.837042	-0.099943
H	2.952460	1.802935	1.170518
O	-3.354021	-0.120121	-1.520839
H	-3.159137	-1.062001	-1.420417
H	-4.318152	-0.066909	-1.569647
O	3.578767	-0.728538	-0.736529
H	3.170565	-0.641423	-1.608964
H	4.512537	-0.520723	-0.876718

Table S12: Optimized geometry for the TS of the reaction via the H_3O^+ with five explicit solvent molecules added.

C	0.311978	-1.086899	-0.949123
H	-0.645146	-0.651353	-1.247148
H	0.514795	-1.950137	-1.586544
H	1.098231	-0.344241	-1.111126
C	0.278752	-1.541894	0.517227
H	-0.547447	-2.256616	0.649936
H	1.205816	-2.033611	0.821951
C	-0.051431	-0.442664	1.439409
H	-0.940734	0.144693	1.214524
C	0.770932	0.013507	2.459166
H	0.374573	0.727807	3.176559
H	1.645450	-0.570840	2.735482
H	1.066044	0.723147	1.523824
O	1.135231	2.046042	0.303172
H	1.781857	1.834963	-0.401908
H	0.248540	1.988609	-0.107982
O	-1.491641	1.834619	-0.722679
H	-2.058242	1.081204	-0.456833
O	3.093341	1.345977	-1.562953
H	3.331889	0.522895	-1.087615
H	2.651728	1.055822	-2.371923
H	-2.008052	2.628443	-0.532383
O	-3.089089	-0.379499	-0.015903
H	-2.869522	-1.064638	-0.661692
H	-2.914383	-0.783636	0.857324
O	3.649972	-0.866847	0.022392
H	3.206926	-1.637924	-0.358580
O	-2.358452	-1.422840	2.502646
H	-2.465509	-0.754707	3.193959
H	3.171774	-0.688746	0.844566
H	-2.887078	-2.176796	2.797948

Table S13: Optimized geometry for the TS of the reaction via the H_3O^+ with six explicit solvent molecules added.

C	0.634912	0.193769	-1.781157
H	1.694622	0.422579	-1.634181
H	0.334016	0.548553	-2.769128
H	0.505607	-0.890246	-1.749449
C	-0.226436	0.880557	-0.712721
H	-0.093950	1.970553	-0.798157
H	-1.291711	0.662940	-0.831328
C	0.217867	0.566671	0.654263
H	1.291448	0.600803	0.847010
C	-0.606971	0.038053	1.644931
H	-0.220696	-0.017977	2.659169
H	-1.684048	0.135324	1.516407
H	-0.347665	-1.020361	1.141951
O	-0.170339	-2.533670	0.373602
H	-0.781011	-2.355261	-0.373810
H	0.743446	-2.391491	0.044628
O	2.485612	-2.066384	-0.268914
H	2.838937	-1.166756	-0.100700
O	-2.094016	-1.856169	-1.503325
H	-2.614073	-2.638819	-1.728328
H	-2.698372	-1.283396	-0.986828
H	3.008449	-2.653363	0.292850
O	3.651379	0.393745	0.295461
H	4.584167	0.371667	0.045535
H	3.302213	1.247990	-0.041734
O	2.573129	2.811817	-0.470434
H	2.115893	2.742576	-1.319294
H	1.868039	2.967167	0.190309
O	-3.781246	-0.230671	0.016474
H	-3.470560	0.685095	0.022790
H	-4.665140	-0.192767	-0.373369
O	0.537318	3.049426	1.426557
H	-0.203278	3.606508	1.149281
H	0.783473	3.368802	2.305526

Table S14: Optimized geometry for the TS of the reaction via the H_3O^+ with seven explicit solvent molecules added.

C	0.409634	0.004482	-1.232263
C	0.405767	-0.674093	0.142743
C	-0.683219	-0.201780	1.007946
C	-0.516585	0.249666	2.317344
O	0.112335	2.807963	0.949746
O	2.663884	1.765136	0.870767
O	3.666748	-0.014003	-1.033746
O	-1.626722	2.586532	-1.207909
O	-3.281460	0.357660	-1.170483
O	-2.286300	-2.200728	-1.251563
H	-0.591845	-0.007880	-1.673036
H	1.090372	-0.524407	-1.902309
H	0.740342	1.043423	-1.149075
H	0.171383	-1.745978	0.017039
H	1.369380	-0.609956	0.656874
H	-1.662258	-0.064064	0.544229
H	-1.404465	0.403550	2.925293
H	0.416981	0.017663	2.826375
H	-0.329599	1.294071	1.775910
H	1.016503	2.493894	0.740804
H	-0.425442	2.714904	0.134995
H	-2.157845	1.761724	-1.204400
H	3.324661	2.467250	0.931441
H	2.994861	1.153318	0.180927
H	-2.269489	3.300275	-1.102303
H	-3.986174	0.457401	-1.823540
H	-2.931531	-0.553420	-1.287837
H	-1.429514	-2.243201	-1.697191
H	-2.101939	-2.368699	-0.304699
H	3.232673	-0.872434	-0.931212
H	4.594414	-0.175649	-0.814535
O	-1.905210	-2.615387	1.475137
H	-1.034623	-2.766973	1.901086
H	-2.454562	-2.165353	2.130365
O	0.640701	-2.925167	2.494710
H	1.224639	-3.120493	1.748748
H	0.746329	-3.671481	3.099830

Table S15: Optimized geometry for the reactants of the reaction via the HCl.

C	1.569705	-1.557947	0.118542
C	1.876564	-0.140299	-0.371648
C	1.142152	0.900697	0.420621
C	0.355073	1.848722	-0.100949
H	1.808976	-1.662319	1.181703
H	2.155770	-2.296895	-0.434674
H	0.510171	-1.799641	-0.013222
H	2.954138	0.042401	-0.271915
H	1.626676	-0.037348	-1.433364
H	1.270328	0.855706	1.503627
H	-0.145730	2.579432	0.528432
H	0.205200	1.928173	-1.176575
H	-1.157869	0.276884	0.090029
Cl	-2.287566	-0.364320	-0.021967

Table S16: Optimized geometry for the product of the reaction via the HCl.

C	2.189207	-0.224083	0.112439
C	1.066123	0.711529	-0.318328
C	-0.266054	0.450256	0.364773
C	-1.337220	1.452649	-0.015102
H	2.320225	-0.199337	1.199541
H	3.135042	0.072703	-0.348561
H	1.981252	-1.256920	-0.180748
H	1.332655	1.746108	-0.068113
H	0.922185	0.672756	-1.404773
H	-0.135071	0.409023	1.448551
H	-1.010424	2.451027	0.293249
H	-1.494175	1.458283	-1.097941
H	-2.285664	1.231842	0.479499
Cl	-0.863433	-1.231035	-0.069612

Table S17: Optimized geometry for the reactants of the reaction via the H_3O^+ without explicit solvent molecules added.

C	1.498771	-1.257696	-0.023077
C	1.520550	0.266922	-0.167393
C	0.321014	0.904654	0.467211
C	-0.604103	1.622101	-0.185032
O	-2.058646	-0.999111	-0.044391
H	1.404494	-1.549641	1.027916
H	2.419710	-1.697594	-0.415048
H	0.655365	-1.687935	-0.571540
H	2.418617	0.659845	0.324524
H	1.572609	0.549971	-1.223757
H	0.207291	0.748058	1.541788
H	-1.445097	2.070259	0.337943
H	-0.522790	1.803968	-1.254880
H	-1.415866	-0.224915	-0.045905
H	-2.733478	-0.861982	-0.739259
H	-2.509078	-1.033036	0.823092

Table S18: Optimized geometry for the product of the reaction via the H_3O^+ without explicit solvent molecules added.

C	-2.069108	-0.073789	0.096909
C	-0.739984	-0.717781	-0.285854
C	0.469915	-0.078112	0.360751
C	1.790373	-0.708536	-0.001047
O	0.584544	1.364969	-0.077042
H	-2.187970	-0.038691	1.184336
H	-2.900359	-0.649977	-0.316315
H	-2.157068	0.945709	-0.292626
H	-0.725348	-1.764195	0.037801
H	-0.598757	-0.716703	-1.373352
H	0.345806	0.029427	1.439656
H	1.784733	-1.742340	0.352235
H	1.930565	-0.713791	-1.086331
H	2.620499	-0.181583	0.473070
H	0.664814	1.457356	-1.048760
H	-0.160445	1.924335	0.222071

Table S19: Optimized geometry for the reactants of the reaction via the H_3O^+ with one explicit solvent molecule added.

C	-0.551565	1.760848	0.637694
C	-1.225512	0.928483	-0.455819
C	-1.710331	-0.396401	0.056981
C	-1.444026	-1.578530	-0.510374
O	1.356916	-1.167940	0.858345
H	-1.251478	1.965414	1.454218
H	-0.207035	2.719790	0.240372
H	0.311106	1.237497	1.062001
H	-2.086443	1.488318	-0.843219
H	-0.542485	0.766891	-1.297209
H	-2.321645	-0.366740	0.960609
H	-1.830852	-2.506360	-0.098469
H	-0.844779	-1.644451	-1.417421
H	0.403495	-1.293809	0.653348
H	1.799514	-0.431693	0.135770
H	1.793834	-2.033884	0.781776
O	2.261894	0.442749	-0.703032
H	3.193878	0.276259	-0.915534
H	2.221009	1.337898	-0.329635

Table S20: Optimized geometry for the products of the reaction via the H_3O^+ with one explicit solvent molecule added.

C	-1.605762	1.520887	0.075528
C	-1.133728	0.251138	-0.626290
C	-0.554291	-0.792095	0.314779
C	-0.047000	-2.030463	-0.388818
O	0.606165	-0.231928	1.046314
H	-2.330280	1.285661	0.862084
H	-2.085059	2.197348	-0.636369
H	-0.770264	2.062686	0.531675
H	-1.974022	-0.229231	-1.139123
H	-0.385074	0.487631	-1.393172
H	-1.268905	-1.046703	1.101070
H	-0.874849	-2.501491	-0.924313
H	0.728974	-1.766142	-1.114149
H	0.360357	-2.747879	0.326970
H	1.330220	0.284950	0.378166
H	0.326010	0.382354	1.747776
O	2.170690	0.867281	-0.444991
H	2.988952	1.130877	0.004990
H	1.783792	1.680315	-0.807379

Table S21: Optimized geometry for the reactants of the reaction via the H_3O^+ with two explicit solvent molecules added.

C	-2.240886	0.957392	0.603498
C	-2.075761	-0.092706	-0.498277
C	-1.627832	-1.415269	0.054154
C	-0.593656	-2.127511	-0.406166
O	1.189620	0.208722	0.762737
O	3.382147	-0.676302	0.000586
O	0.518387	2.202552	-0.585560
H	-3.004965	0.645874	1.322736
H	-2.545756	1.920262	0.182727
H	-1.305062	1.103369	1.153480
H	-3.040273	-0.227954	-1.004047
H	-1.359774	0.248151	-1.254867
H	-2.200054	-1.799046	0.900473
H	-0.317574	-3.079374	0.038315
H	-0.004841	-1.783570	-1.255677
H	0.516167	-0.492931	0.641072
H	0.901701	1.048444	0.208773
H	2.116904	-0.153631	0.426100
H	4.122301	-0.302465	0.501313
H	-0.187181	2.714569	-0.162337
H	1.254304	2.819705	-0.710228
H	3.561692	-0.472620	-0.929193

Table S22: Optimized geometry for the products of the reaction via the H_3O^+ with two explicit solvent molecules added.

C	2.357086	-0.297241	-1.113486
C	1.726547	-0.548750	0.252295
C	0.247266	-0.885702	0.186246
C	-0.397550	-1.047953	1.548008
O	-0.428847	0.188411	-0.552674
O	-2.821903	-0.443207	-0.808322
O	-0.003730	2.388027	0.565444
H	2.181005	-1.142943	-1.786485
H	3.437217	-0.159371	-1.018461
H	1.945510	0.600897	-1.582909
H	2.217025	-1.394376	0.746035
H	1.864068	0.321911	0.906409
H	0.088741	-1.773282	-0.432740
H	0.080291	-1.874584	2.080624
H	-0.274024	-0.134919	2.139130
H	-1.464705	-1.269142	1.453905
H	-0.273412	1.114857	-0.098829
H	-1.448767	-0.019485	-0.656204
H	-3.324620	0.141816	-1.394012
H	0.948638	2.487423	0.716072
H	-0.260334	3.138454	0.008856
H	-3.280886	-0.425226	0.044638

Table S23: Optimized geometry for the reactants of the reaction via the H_3O^+ with three explicit solvent molecules added.

C	1.856274	0.433136	1.367576
C	1.900972	1.112330	-0.004774
C	0.810231	2.133005	-0.154327
C	-0.100482	2.154340	-1.132340
O	-1.498643	-0.111599	0.612418
O	-0.232110	-1.481523	-0.963735
O	2.063024	-2.496000	-0.066174
O	-3.988067	-0.335498	0.366013
H	1.864434	1.181878	2.166552
H	2.721177	-0.220024	1.514190
H	0.949122	-0.168983	1.478820
H	2.869402	1.616278	-0.117526
H	1.826404	0.368637	-0.807728
H	0.777741	2.906235	0.615388
H	-0.861914	2.927989	-1.180913
H	-0.100781	1.404280	-1.921999
H	-1.245406	0.813615	0.428698
H	-0.936879	-0.733394	-0.076732
H	-2.521288	-0.218825	0.487324
H	-4.357905	-0.960932	1.006086
H	0.000395	-0.933606	-1.728497
H	0.626095	-1.835154	-0.605364
H	-4.256014	-0.663309	-0.504615
H	2.312170	-3.234540	-0.639044
H	2.777649	-1.850046	-0.159632

Table S24: Optimized geometry for the products of the reaction via the H_3O^+ with three explicit solvent molecules added.

C	1.353190	-1.669752	-1.079106
C	0.688460	-1.500841	0.283309
C	-0.752904	-1.027016	0.199398
C	-1.398751	-0.813215	1.554316
O	-0.769810	0.230226	-0.552976
O	0.704232	1.876564	0.515917
O	3.167491	1.089958	-0.148222
O	-3.164533	0.919577	-0.855569
H	0.784348	-2.363658	-1.706798
H	2.365506	-2.068417	-0.967467
H	1.425985	-0.715869	-1.609605
H	0.676672	-2.455749	0.819434
H	1.256079	-0.794841	0.903836
H	-1.341993	-1.718834	-0.409939
H	-1.418653	-1.757370	2.105143
H	-0.828464	-0.081362	2.136364
H	-2.426227	-0.454226	1.444698
H	-0.152084	0.971047	-0.077982
H	-1.739946	0.567420	-0.675737
H	-3.295376	1.601151	-1.530829
H	0.602684	1.827917	1.478211
H	1.638535	1.600294	0.318044
H	-3.540767	1.279911	-0.039166
H	3.868330	1.546008	0.337589
H	3.286372	0.150926	0.053500

Table S25: Optimized geometry for the reactants of the S_N2 reaction without explicit solvent molecules added.

C	-0.985093	2.073201	0.045161
C	-0.789578	0.758586	0.795795
C	-0.746580	-0.464331	-0.090530
C	-0.549298	-1.764217	0.643614
O	-2.112212	-0.568667	-0.759284
H	-0.238878	2.184198	-0.748439
H	-0.877447	2.918005	0.729883
H	-1.980989	2.146745	-0.404431
H	0.179543	0.766242	1.305348
H	-1.564200	0.618233	1.558021
H	-0.037556	-0.345110	-0.911123
H	0.455194	-1.747414	1.073173
H	-1.282482	-1.876648	1.446900
H	-0.615111	-2.618578	-0.036253
H	-2.264172	0.140531	-1.417409
H	-2.216249	-1.420741	-1.230376
Cl	2.691961	0.009673	-0.215015

Table S26: Optimized geometry for the TS of the S_N2 reaction without explicit solvent molecules added.

C	-0.660643	2.109381	0.022024
C	-0.552925	0.817961	0.819288
C	-0.333271	-0.393255	-0.012396
C	-0.259492	-1.728932	0.629235
O	-2.378009	-0.580002	-0.614210
H	0.254451	2.276397	-0.553719
H	-0.807010	2.961068	0.690391
H	-1.505611	2.074714	-0.672431
H	0.280783	0.858275	1.529068
H	-1.449172	0.632047	1.422905
H	-0.150051	-0.289025	-1.071801
H	0.542462	-1.716066	1.371865
H	-1.193945	-1.914260	1.168323
H	-0.077154	-2.523228	-0.094120
H	-2.554759	0.081072	-1.301117
H	-2.459035	-1.435414	-1.063692
Cl	2.293006	-0.070382	-0.309465

Table S27: Optimized geometry for the products of the S_N2 reaction without explicit solvent molecules added.

C	-0.343887	2.091309	0.166059
C	-0.208936	0.764589	0.903399
C	0.237619	-0.394431	0.027260
C	0.202113	-1.729193	0.743075
O	-3.193701	-0.486418	-0.634541
H	0.619057	2.427715	-0.229165
H	-0.722690	2.867866	0.835940
H	-1.042333	2.001658	-0.673693
H	0.481783	0.856591	1.749988
H	-1.182845	0.472745	1.317066
H	-0.354915	-0.429024	-0.890718
H	0.829497	-1.705715	1.639335
H	-0.829226	-1.935973	1.049625
H	0.539349	-2.541020	0.094881
H	-2.612634	0.269737	-0.793023
H	-2.595777	-1.203256	-0.384073
Cl	1.946993	-0.093154	-0.569329

Table S28: Optimized geometry for the reactants of the S_N2 reaction with one explicit solvent molecule added.

C	0.315591	2.110374	-0.024882
C	0.249692	0.776928	-0.762583
C	0.187133	-0.426614	0.161440
C	0.185642	-1.751223	-0.565081
O	1.372851	-0.452465	1.056962
O	3.442503	-0.183301	-0.195525
H	-0.534327	2.219747	0.657543
H	0.290713	2.943510	-0.731806
H	1.237222	2.201976	0.560090
H	-0.658232	0.732417	-1.373633
H	1.105981	0.664198	-1.439589
H	-0.666707	-0.346111	0.837225
H	-0.696083	-1.798363	-1.209120
H	1.078963	-1.849727	-1.190256
H	0.146375	-2.584903	0.139947
H	2.319569	-0.318857	0.518185
H	1.306469	0.222839	1.755609
H	3.577810	0.744008	-0.447574
H	4.227325	-0.446086	0.310169
Cl	-3.346250	-0.091489	0.109903

Table S29: Optimized geometry for the TS of the S_N2 reaction with one explicit solvent molecule added.

C	0.522672	1.848153	0.219959
C	0.176642	0.658847	-0.663435
C	-0.377758	-0.503722	0.080533
C	-0.647482	-1.774692	-0.635389
O	1.497563	-1.153857	0.940097
O	3.489872	0.194840	-0.387288
H	-0.372636	2.215632	0.730450
H	0.936282	2.664387	-0.377335
H	1.261416	1.569251	0.978144
H	-0.572403	0.928200	-1.415829
H	1.045117	0.298583	-1.228604
H	-0.633999	-0.399762	1.123649
H	-1.313378	-1.572300	-1.477943
H	0.293733	-2.149421	-1.048245
H	-1.093780	-2.525718	0.015487
H	2.231752	-0.673176	0.491195
H	1.501645	-0.828721	1.852108
H	3.255536	1.132285	-0.437519
H	4.336653	0.171481	0.078877
Cl	-2.871756	0.321759	0.134299

Table S30: Optimized geometry for the products of the S_N2 reaction with one explicit solvent molecule added.

C	-0.397025	-1.711336	0.270032
C	0.007452	-0.565551	-0.649460
C	0.961111	0.435421	-0.017841
C	1.218207	1.644594	-0.893316
O	-2.198900	1.403838	1.148830
O	-3.454007	-0.375155	-0.633575
H	0.471057	-2.306320	0.569053
H	-1.099474	-2.384234	-0.231136
H	-0.876554	-1.332469	1.179954
H	0.458039	-0.947390	-1.573325
H	-0.882810	0.005704	-0.942061
H	0.604531	0.739612	0.968968
H	1.602601	1.340220	-1.871568
H	0.271798	2.175187	-1.041267
H	1.930183	2.330897	-0.429643
H	-2.611425	0.772514	0.527346
H	-1.586225	0.872096	1.672680
H	-3.037853	-1.243728	-0.545252
H	-4.375576	-0.512766	-0.376456
Cl	2.565676	-0.385739	0.336128

Table S31: Optimized geometry for the reactants of the S_N2 reaction with two explicit solvent molecules added.

C	-0.243871	0.213878	1.920452
C	-0.967513	-0.920151	1.200255
C	-0.656050	-0.992318	-0.287470
C	-1.459503	-2.045663	-1.018823
O	-0.923339	0.298835	-0.932507
O	1.067659	1.702285	-0.698239
O	-3.052672	1.348165	-0.059243
H	0.837736	0.153433	1.754107
H	-0.428836	0.166623	2.996888
H	-0.585768	1.192539	1.567538
H	-0.673838	-1.885227	1.627729
H	-2.053836	-0.832340	1.333779
H	0.418964	-1.141781	-0.436333
H	-1.262250	-3.026932	-0.578950
H	-2.530439	-1.835767	-0.929260
H	-1.190853	-2.076878	-2.077372
H	-1.787374	0.740088	-0.579990
H	-0.075276	0.957769	-0.837493
H	1.311086	2.119384	-1.537917
H	-3.072272	1.256728	0.905465
H	-3.084526	2.301101	-0.229932
H	1.822073	1.089225	-0.460549
Cl	3.269639	-0.206277	0.006807

Table S32: Optimized geometry for the TS of the S_N2 reaction with two explicit solvent molecules added.

C	-0.418011	0.103957	1.827133
C	0.061970	-0.932831	0.822257
C	0.541703	-0.355265	-0.463653
C	0.896898	-1.260213	-1.586242
O	-1.424783	0.165668	-1.234899
O	-1.205789	2.772869	-0.305857
O	-3.242988	-1.248308	0.326399
H	0.377645	0.824368	2.043446
H	-0.709011	-0.375658	2.764972
H	-1.284632	0.650675	1.441481
H	0.891688	-1.521761	1.226941
H	-0.724239	-1.657689	0.578937
H	0.660700	0.712951	-0.562293
H	1.641214	-1.982430	-1.242400
H	0.004836	-1.823961	-1.874287
H	1.283376	-0.714170	-2.446219
H	-2.096811	-0.314056	-0.703569
H	-1.486314	1.105447	-0.961773
H	-0.797353	3.374007	-0.943454
H	-3.069436	-1.025614	1.251738
H	-4.165572	-1.000778	0.177617
H	-0.535745	2.641094	0.379736
Cl	2.970751	0.132461	0.293353

Table S33: Optimized geometry for the products of the S_N2 reaction with two explicit solvent molecules added.

C	0.439264	-0.450936	-1.653803
C	-0.131401	-1.213235	-0.463424
C	-1.007333	-0.378023	0.456456
C	-1.424966	-1.113887	1.712755
O	2.077284	0.852814	1.312101
O	0.575230	2.775090	-0.190516
O	3.315354	-1.211473	-0.202902
H	-0.355529	-0.015545	-2.267311
H	1.023095	-1.117796	-2.296096
H	1.096558	0.359985	-1.320076
H	-0.703630	-2.086623	-0.798476
H	0.690461	-1.590671	0.158793
H	-0.515257	0.564680	0.703598
H	-1.950699	-2.040713	1.463977
H	-0.525471	-1.366844	2.283748
H	-2.070333	-0.496493	2.341544
H	2.455349	0.167149	0.731182
H	1.567041	1.448552	0.734024
H	-0.015010	3.200673	0.446175
H	2.930727	-1.243444	-1.089595
H	4.244813	-0.985813	-0.342089
H	-0.014317	2.340496	-0.822272
Cl	-2.520831	0.145144	-0.446382

Table S34: Optimized geometry for the reactants of the S_N2 reaction with three explicit solvent molecules added.

C	0.314495	-0.574920	-1.536466
C	0.060365	-1.063148	-0.113463
C	-0.426186	0.030544	0.824488
C	-0.603326	-0.441261	2.250924
O	0.528149	1.148476	0.847479
O	2.868979	0.381211	0.900914
O	3.486375	-1.461733	-0.970619
O	-0.057294	2.729606	-1.013739
H	-0.580754	-0.096057	-1.949244
H	0.578479	-1.408663	-2.194243
H	1.134432	0.151948	-1.569298
H	-0.715924	-1.836006	-0.116562
H	0.967153	-1.519498	0.306467
H	-1.355679	0.460357	0.440310
H	-1.328513	-1.259401	2.274387
H	0.346342	-0.808181	2.654328
H	-0.971419	0.367588	2.886895
H	1.544152	0.822078	0.849663
H	0.349363	1.804498	0.069291
H	0.439800	3.560325	-1.000638
H	3.492884	1.108737	0.764349
H	3.072971	-0.296611	0.207616
H	0.102411	2.339285	-1.885727
H	2.700438	-1.845032	-1.384602
H	3.940261	-2.206551	-0.552606
Cl	-3.788127	-0.554505	-0.380327

Table S35: Optimized geometry for the TS of the S_N2 reaction with three explicit solvent molecules added.

C	0.400433	-0.395668	-1.484317
C	-0.045931	-0.919801	-0.126785
C	-0.967743	-0.006787	0.604807
C	-1.339771	-0.313621	2.009956
O	0.538223	1.483849	1.103856
O	3.036455	0.358753	0.846740
O	3.232856	-1.993295	-0.639304
O	-0.063989	3.059808	-1.099067
H	-0.466988	-0.095558	-2.081420
H	0.939715	-1.168293	-2.038057
H	1.062709	0.468411	-1.372646
H	-0.572896	-1.874453	-0.225956
H	0.807275	-1.119505	0.534116
H	-1.381661	0.854859	0.104612
H	-1.730498	-1.332594	2.064253
H	-0.435370	-0.278102	2.624271
H	-2.078392	0.385725	2.400430
H	1.427682	1.074616	1.000375
H	0.441454	2.107163	0.353139
H	0.366937	3.921168	-1.179238
H	3.640398	0.973364	0.409660
H	3.072802	-0.465623	0.318345
H	0.185611	2.577324	-1.899370
H	2.404038	-2.484865	-0.720034
H	3.839518	-2.597295	-0.190192
Cl	-3.161919	-0.847294	-0.460121

Table S36: Optimized geometry for the Product of the S_N2 reaction with three explicit solvent molecules added.

C	0.432177	-0.244783	-1.413452
C	0.073119	-0.942896	-0.107273
C	-1.226606	-0.474336	0.526383
C	-1.501974	-1.123598	1.866934
O	0.956643	2.109881	1.256111
O	3.174716	0.836127	0.046978
O	3.240924	-1.941148	-0.288374
O	-1.179632	2.855242	-0.504629
H	-0.323229	-0.427897	-2.183264
H	1.392681	-0.606250	-1.792710
H	0.517531	0.836938	-1.263179
H	0.027150	-2.031054	-0.247425
H	0.854588	-0.748413	0.640043
H	-1.237525	0.613996	0.612624
H	-1.527507	-2.213407	1.772367
H	-0.696021	-0.853764	2.557426
H	-2.448780	-0.781100	2.290199
H	1.657852	1.613001	0.793010
H	0.289079	2.333749	0.583109
H	-1.058913	3.705497	-0.948278
H	3.180635	1.204137	-0.846519
H	3.144158	-0.134728	-0.076923
H	-1.306986	2.216082	-1.219519
H	2.360393	-2.338987	-0.244673
H	3.728007	-2.332261	0.449521
Cl	-2.632625	-0.836629	-0.599532