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Supplementary Information

Ab Initio and CVTST Investigation of the Gas Phase Nucleophilic Substitution $CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$.

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Table S1. Molecular properties at the MP2/6-31+G(d) level for CH_3Cl: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	0.000000	0.000000	–1.123355
H	0.000000	1.030469	–1.475110
H	0.892412	–0.515235	–1.475110
H	–0.892412	–0.515235	–1.475110
Cl	0.000000	0.000000	0.656792

Frequencies (cm^{-1}): 779.29; 1078.32; 1078.32; 1464.02; 1528.34; 1528.34; 3142.51; 3253.09; 3253.09
E = –499.35746797637 hartrees

Table S2. Molecular properties at the MP2/6-31+G(d) level for OH^-: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
O	0.000000	0.000000	0.108608
H	0.000000	0.000000	–0.868863

Frequencies (cm^{-1}): 3701.26
E = –75.588364152575 hartrees

Table S3. Molecular properties at the MP2/6-31+G(d) level for the pre-barrier complex: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	0.033971	0.760034	–0.000101
H	0.091140	1.381038	0.893870
H	0.091471	1.381683	–0.893603
H	–0.892747	0.152698	–0.000582
Cl	1.503467	–0.294984	0.000020
O	–2.713017	–0.191125	0.000236
H	–3.348501	–0.931890	–0.001308

Frequencies (cm^{-1}): 72.80; 78.31; 216.60; 240.76; 276.21; 715.76; 1091.47; 1092.73; 1490.21; 1525.38; 1553.35; 2926.09; 3178.53; 3235.52; 3728.65
E = –574.97140057471 hartrees

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Table S4. Molecular properties at the MP2/6-31+G(d) level for the saddle point: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	–0.421165	–0.022112	0.000009
H	–0.567399	–0.550420	–0.924724
H	–0.567398	–0.550452	0.924724
H	–0.606688	1.036758	0.000033
Cl	1.659699	0.001709	–0.000003
O	–2.610864	0.115196	–0.000005
H	–3.059501	–0.753832	–0.000001

Frequencies (cm^{-1}): *499.57* ***i***; 97.15; 220.12; 231.39; 289.1; 538.91; 1015.16; 1023.98; 1180.64; 1446.72; 1452.61; 3250.17; 3441.19; 3442.32; 3701.10
E = –574.96322199139 hartrees

Table S5. Molecular properties at the MP2/6-31+G(d) level for the post-barrier complex: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	–1.902537	–0.516001	0.000000
H	–1.610903	–1.091300	0.888816
H	–1.610902	–1.091300	–0.888815
H	–2.990023	–0.388489	–0.000001
Cl	1.682197	–0.071835	0.000000
O	–1.328536	0.780220	0.000000
H	–0.342008	0.646531	0.000000

Frequencies (cm^{-1}): 103.92; 112.02; 206.90; 815.34; 1101.00; 1149.44; 1197.87; 1492.14; 1513.83; 1539.10; 1565.92; 3052.21; 3118.42; 3153.77; 3366.64
E = –575.05473506618 hartrees

Table S6. Molecular properties at the MP2/6-31+G(d) level for CH_3OH and Cl^-: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	0.672965	–0.020775	0.00000
H	1.025985	–0.546617	–0.89422
H	1.075795	0.991382	–0.00110
H	1.026139	–0.544749	0.89526
O	–0.751548	0.123279	0.00000
H	–1.153324	–0.761600	0.00000

Frequencies (cm^{-1}): 332.74; 1063.72; 1089.48; 1196.40; 1384.67; 1523.34; 1551.47; 1561.66; 3083.24; 3155.83; 3227.86; 3775.10
E (CH_3OH) = -115.35783874302 hartrees
E (Cl^-) = –459.67114538150 hartrees

Table S7. Molecular properties at the MP2/aug-cc-pVDZ level for CH_3Cl: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	0.000000	0.000000	–1.135417
H	0.000000	1.041079	–1.478351
H	–0.901601	–0.520540	–1.478351
H	0.901601	–0.520540	–1.478351
Cl	0.000000	0.000000	0.661621

Frequencies (cm^{-1}): 749.91; 1032.75; 1032.75; 1368.47; 1472.80; 1472.80; 3104.39; 3224.21; 3224.21
E = –499.42531361020 hartrees

Table S8. Molecular properties at the MP2/ aug-cc-pVDZ level for OH^-: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
O	0.000000	0.000000	0.108143
H	0.000000	0.000000	–0.865142

Frequencies (cm^{-1}): 3764.12
E = –75.637017913898 hartrees

Table S9. Molecular properties at the MP2/aug-cc-pVDZ level for the pre-barrier complex: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	0.008860	0.784627	0.000121
H	0.092554	1.406363	0.901240
H	0.092292	1.406292	–0.901069
H	–0.932778	0.170534	0.000274
Cl	1.482799	–0.300411	–0.000032
O	–2.662117	–0.198563	–0.000267
H	–3.215864	–0.995461	0.001518

Frequencies (cm^{-1}): 59.44; 65.50; 193.14; 245.53; 259.86; 678.83; 1039.04; 1051.64; 1402.60; 1467.73; 1492.54; 2743.36; 3132.31; 3197.59; 3792.84
E = –575.08846066798 hartrees

Table S10. Molecular properties at the MP2/aug-cc-pVDZ level for the saddle point: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	0.398333	–0.014578	0.000001
H	0.566164	–0.545574	0.929426
H	0.566137	–0.546251	–0.929038
H	0.589457	1.052550	–0.000414
Cl	–1.657859	0.000015	0.000001
O	2.631868	0.113193	0.000004
H	3.016894	–0.779054	–0.000019

Frequencies (cm^{-1}): *423.97* ***i***; 112.34; 204.68; 219.10; 292.07; 480.98; 979.71; 989.88; 1138.64; 1406.14; 1409.85; 3200.41; 3391.74; 3397.28; 3780.51
E = –575.08370770211 hartrees

Table S11. Molecular properties at the MP2/aug-cc-pVDZ level for the post-barrier complex: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	–1.853131	–0.522400	0.000000
H	–1.544917	–1.098629	0.892558
H	–1.544916	–1.098629	–0.892558
H	–2.952780	–0.431222	–0.000001
Cl	1.645109	–0.071149	0.000000
O	–1.310013	0.789362	0.000000
H	–0.325347	0.657525	0.000000

Frequencies (cm^{-1}): 83.93; 107.70; 207.54; 786.55; 1080.26; 1118.71; 1170.63; 1447.25; 1473.62; 1474.26; 1510.12; 3013.50; 3081.92; 3112.53; 3318.72
E = –575.17064019993 hartrees

Table S12. Molecular properties at the MP2/aug-cc-pVDZ level for CH_3OH and Cl^-: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	–0.046876	0.671460	0.000000
H	–1.100257	0.979177	0.000000
H	0.442061	1.081661	0.899552
H	0.442061	1.081661	–0.899552
O	–0.046876	–0.763901	0.000000
H	0.872403	–1.060049	0.000000

Frequencies (cm^{-1}): 312.19; 1042.96; 1074.60; 1168.90; 1366.43; 1464.64; 1493.47; 1504.96; 3053.49; 3131.28; 3190.23; 3840.86
E (CH_3OH)= -115.42193115131 hartrees
E (Cl^-) = –459.72276445242 hartrees

Table S13. Molecular properties at the BHandHLYP/6-31+G(d) level for CH_3Cl: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	0.000000	0.000000	–1.127866
H	0.000000	1.025251	–1.472241
H	–0.887893	–0.512626	–1.472241
H	0.887893	–0.512626	–1.472241
Cl	0.000000	0.000000	0.657878

Frequencies (cm^{-1}): 760.10; 1086.27; 1086.27; 1469.86; 1557.93; 1557.93; 3191.91; 3293.44; 3293.44
E = –500.065255455 hartrees

Table S14. Molecular properties at the BHandHLYP/6-31+G(d) level for OH^-: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
O	0.000000	0.000000	0.106873
H	0.000000	0.000000	–0.854988

Frequencies (cm^{-1}): 3830.23
E = –75.7456600913 hartrees

Table S15. Molecular properties at the BHandHLYP/6-31+G(d) level for the pre-barrier complex: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	–0.014882	0.789670	0.000019
H	–0.097696	1.401913	–0.888951
H	–0.097702	1.401823	0.889070
H	0.921520	0.195411	–0.000063
Cl	–1.478102	–0.302100	–0.000006
O	2.669380	–0.195915	–0.000040
H	3.135852	–1.034152	0.000250

Frequencies (cm^{-1}): 83.04; 90.76; 235.23; 267.49; 272.63; 667.81; 1101.38; 1103.95; 1502.65; 1553.19; 1585.80; 2843.49; 3217.61; 3273.42; 3885.01
E = –575.837982776 hartrees

Table S16. Molecular properties at the BHandHLYP/6-31+G(d) level for the saddle point: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	0.368836	–0.026113	0.000000
H	0.558067	–0.549433	0.911975
H	0.558068	–0.549470	–0.911954
H	0.597671	1.017821	–0.000021
Cl	–1.666157	0.003070	0.000000
O	2.657935	0.113323	0.000000
H	3.134366	–0.721025	0.000000

Frequencies (cm^{-1}): *352.23* ***i***; 34.01; 193.41; 208.29; 280.67; 448.51; 1007.63; 1007.84; 1217.15; 1480.63; 1484.62; 3309.78; 3483.72; 3484.49; 3862.17
E = –575.835079754 hartrees

Table S17. Molecular properties at the BHandHLYP/6-31+G(d) level for the post-barrier complex: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	1.910468	–0.504102	0.000000
H	1.628532	–1.083354	–0.882117
H	1.628532	–1.083354	0.882117
H	2.992950	–0.379663	0.000000
Cl	–1.691332	–0.070709	0.000000
O	1.334596	0.765697	0.000001
H	0.363042	0.647458	0.000000

Frequencies (cm^{-1}): 81.91; 108.73; 193.57; 798.90; 1159.53; 1174.02; 1230.61; 1520.41; 1547.14; 1563.10; 1590.15; 3088.55; 3131.66; 3160.66; 3541.82
E = –575.934040411 hartrees

Table S18. Molecular properties at the BHandHLYP/6-31+G(d) level for CH_3OH and Cl^-: Coordinates (Å), Vibrational Frequencies (cm^{-1}), Electronic Energies (hartrees)

	X	Y	Z
C	–0.046157	0.659400	0.000000
H	–1.084264	0.970906	0.000000
H	0.438156	1.065895	0.888031
H	0.438156	1.065895	–0.888031
O	–0.046157	–0.748498	0.000000
H	0.854156	–1.071114	0.000000

Frequencies (cm^{-1}): 329.67; 1104.95; 1132.89; 1228.15; 1419.62; 1555.31; 1575.51; 1584.95; 3116.35; 3168.24; 3242.66; 3945.62
E (CH_3OH) = -115.653967512 hartrees
E (Cl^-) = –460.256270161 hartrees

Table S19. Total energies. ACCD, ACCT and ACCQ stand for aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ, respectively

E_{total} / hartrees	MP2/6-31+G(d)	MP2/ACCD	MP2/ACCT[a]	MP2/ACCQ[a]	CCSD(T)/ACCD[a]
CH_3Cl	–499.357468	–499.4253136	–499.5288533	–499.5614937	–499.4647953
OH^-	–75.58836415	–75.63701791	–75.70225633	–75.72490424	–75.64389648
$CH_3Cl + OH^-$	–574.9458321	–575.0623315	–575.2311097	–575.2863979	–575.1086917
$[CH_3Cl\text{---}OH]^-$	–574.9714006	–575.0884607	–575.2564184	–575.3115517	–575.1356182
$[Cl\text{---}CH_3\text{---}OH]^-$	–574.963222	–575.0837077	–575.2499567	–575.3046557	–575.1330561
$[Cl\text{---}CH_3OH]^-$	–575.0547351	–575.1706402	–575.3366364	–575.3919515	–575.2198936
CH_3OH	–115.3578387	–115.4219312	–115.5286432	–115.5625892	–115.4558825
Cl^-	–459.6711454	–459.7227645	–459.7807918	–459.8023747	–459.7383021
$CH_3OH + Cl^-$	–575.0289841	–575.1446956	–575.309435	–575.3649639	–575.1941846

[a]single point calculations at the MP2/ACCD optimized geometries.

Table S20. Relative energies (ΔE and ΔE^0, with vibrational zero point energy corrections). ACCD, ACCT, ACCQ and CBS stand for aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ and complete basis set limit, respectively

ΔE / (kcal mol^{-1})	MP2/6-31+G(d)	MP2/ACCD	MP2/ACCT[a]	MP2/ACCQ[a]	MP2/CBS	CCSD(T)/ACCD[a]	CCSD(T)/CBS
$CH_3Cl + OH$-	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$[CH_3Cl\text{---}OH]$-	–16.04	–16.40	–15.88	–15.78	–15.76	–16.90	–16.26
$[Cl\text{---}CH_3\text{---}OH]$-	–10.91	–13.41	–11.83	–11.46	–11.34	–15.29	–13.22
$[Cl\text{---}CH_3OH]$-	–68.34	–67.96	–66.22	–66.24	–66.23	–69.78	–68.04
$CH_3OH + Cl$–	–52.18	–51.68	–49.15	–49.30	–49.22	–53.65	–51.19
ΔE^0 / (kcal mol^{-1})	MP2/6-31+G(d)	MP2/ACCD	MP2/ACCT[b]	MP2/ACCQ[b]	MP2/CBS[b]	CCSD(T)/ACCD[b]	CCSD(T)/CBS[b]
$CH_3Cl + OH$-	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$[CH_3Cl\text{---}OH]$-	–15.16	–15.86	–15.34	–15.25	–15.22	–16.36	–15.72
$[Cl\text{---}CH_3\text{---}OH]$-	–10.16	–12.62	–11.03	–10.66	–10.55	–14.49	–12.42
$[Cl\text{---}CH_3OH]$–	–64.50	–64.33	–62.59	–62.60	–62.59	–66.15	–64.41
$CH_3OH + Cl$–	–49.12	–48.54	–46.01	–46.16	–46.08	–50.51	–48.05

[a]single point calculations at the MP2/ACCD optimized geometries; [b]vibrational zero-point energies corrections were calculated at the MP2/ACCD level.

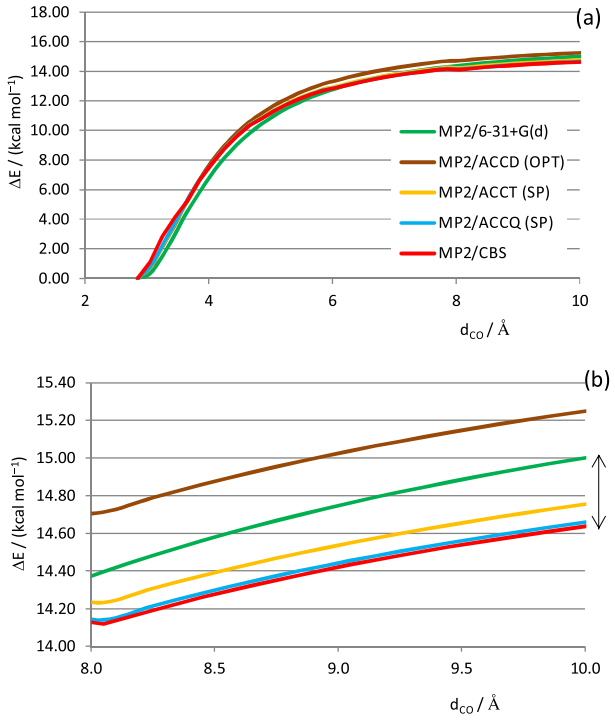

Figure S1. Dissociation curves calculated at the MP2 level with different basis sets, including the complete basis set limit. (a) complete dissociation curve and (b) variational region. The arrow in Figure S1b represents the distance between the MP2/6-31+G(d) and the MP2/CBS curves and color is the same as for Figure S1a.

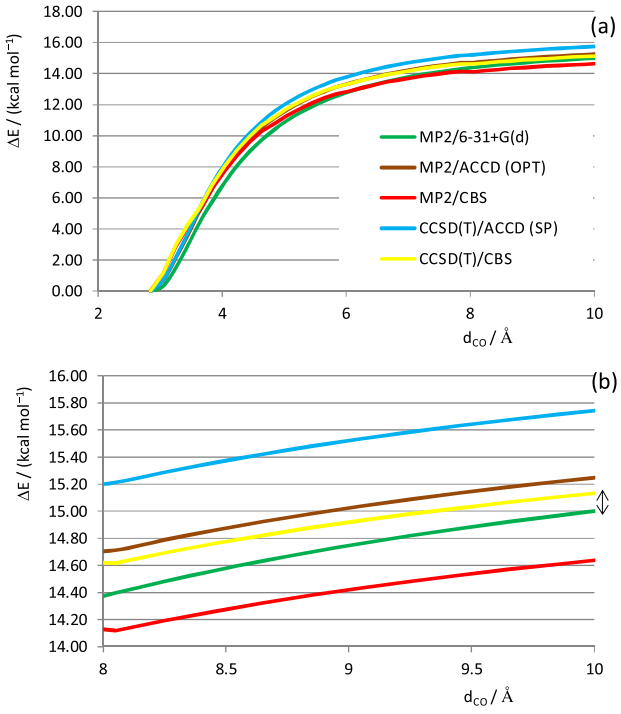

Figure S2. Dissociation curves calculated at the MP2 and CCSD(T) levels with different basis sets, including the complete basis set limit. (a) complete dissociation curve and (b) variational region. The arrow in Figure S2b represents the distance between the MP2/6-31+G(d) and the CCSD(T)/CBS curves and color is the same as for Figure S2a.