

Electronic supplementary information (ESI) for *Chem. Commun.*

**Adequate Representation of Charge Polarization Effects Leads to a
Successful Treatment of the $\text{CF}_4 + \text{SiCl}_4 \rightarrow \text{CCl}_4 + \text{SiF}_4$ Reaction by
Density Functional Theory**

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This ESI contains the geometries (Table ESI-1) and energies of reaction (Table ESI-2) that underlie the results in Table 2 of the paper, which contains enthalpies of reaction at 298 K. Table ESI-3 contains enthalpies of reaction at 0 K.

Table ESI-1. Geometries (Å)

B3LYP/6-311+G(d,p) geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.034330	1.034330	1.034330
Cl	-1.034330	-1.034330	1.034330
Cl	-1.034330	1.034330	-1.034330
Cl	1.034330	-1.034330	-1.034330

CF₄

C	0.000000	0.000000	0.000000
F	0.766967	0.766967	0.766967
F	-0.766967	-0.766967	0.766967
F	-0.766967	0.766967	-0.766967
F	0.766967	-0.766967	-0.766967

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.179801	1.179801	1.179801
Cl	-1.179801	-1.179801	1.179801
Cl	-1.179801	1.179801	-1.179801
Cl	1.179801	-1.179801	-1.179801

SiF₄

Si	0.000000	0.000000	0.000000
F	0.914711	0.914711	0.914711
F	-0.914711	-0.914711	0.914711
F	-0.914711	0.914711	-0.914711
F	0.914711	-0.914711	-0.914711

B3LYP/aug-cc-pVQZ geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.029030	1.029030	1.029030
Cl	-1.029030	-1.029030	1.029030
Cl	-1.029030	1.029030	-1.029030
Cl	1.029030	-1.029030	-1.029030

CF₄

C	0.000000	0.000000	0.000000
F	0.765342	0.765342	0.765342
F	-0.765342	-0.765342	0.765342
F	-0.765342	0.765342	-0.765342
F	0.765342	-0.765342	-0.765342

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.176711	1.176711	1.176711
Cl	-1.176711	-1.176711	1.176711
Cl	-1.176711	1.176711	-1.176711
Cl	1.176711	-1.176711	-1.176711

SiF₄

Si	0.000000	0.000000	0.000000
F	0.905658	0.905658	0.905658
F	-0.905658	-0.905658	0.905658
F	-0.905658	0.905658	-0.905658
F	0.905658	-0.905658	-0.905658

B3LYP/6-311+G(3df,2p) geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.027543	1.027543	1.027543
Cl	-1.027543	-1.027543	1.027543
Cl	-1.027543	1.027543	-1.027543
Cl	1.027543	-1.027543	-1.027543

CF₄

C	0.000000	0.000000	0.000000
F	0.764412	0.764412	0.764412
F	-0.764412	-0.764412	0.764412
F	-0.764412	0.764412	-0.764412
F	0.764412	-0.764412	-0.764412

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.174042	1.174042	1.174042
Cl	-1.174042	-1.174042	1.174042
Cl	-1.174042	1.174042	-1.174042
Cl	1.174042	-1.174042	-1.174042

SiF₄

Si	0.000000	0.000000	0.000000
F	0.906073	0.906073	0.906073
F	-0.906073	-0.906073	0.906073
F	-0.906073	0.906073	-0.906073
F	0.906073	-0.906073	-0.906073

B3LYP/MG3S geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.028380	1.028380	1.028380
Cl	-1.028380	-1.028380	1.028380
Cl	-1.028380	1.028380	-1.028380
Cl	1.028380	-1.028380	-1.028380

CF₄

C	0.000000	0.000000	0.000000
F	0.765102	0.765102	0.765102
F	-0.765102	-0.765102	0.765102
F	-0.765102	0.765102	-0.765102
F	0.765102	-0.765102	-0.765102

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.175062	1.175062	1.175062
Cl	-1.175062	-1.175062	1.175062
Cl	-1.175062	1.175062	-1.175062
Cl	1.175062	-1.175062	-1.175062

SiF₄

Si	0.000000	0.000000	0.000000
F	0.902446	0.902446	0.902446
F	-0.902446	-0.902446	0.902446
F	-0.902446	0.902446	-0.902446
F	0.902446	-0.902446	-0.902446

B3LYP/def2-TZVPP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.028314	1.028314	1.028314
Cl	-1.028314	-1.028314	1.028314
Cl	-1.028314	1.028314	-1.028314
Cl	1.028314	-1.028314	-1.028314

CF₄

C	0.000000	0.000000	0.000000
F	0.765616	0.765616	0.765616
F	-0.765616	-0.765616	0.765616
F	-0.765616	0.765616	-0.765616
F	0.765616	-0.765616	-0.765616

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.175268	1.175268	1.175268
Cl	-1.175268	-1.175268	1.175268
Cl	-1.175268	1.175268	-1.175268
Cl	1.175268	-1.175268	-1.175268

SiF₄

Si	0.000000	0.000000	0.000000
F	0.904970	0.904970	0.904970
F	-0.904970	-0.904970	0.904970
F	-0.904970	0.904970	-0.904970
F	0.904970	-0.904970	-0.904970

B3LYP/aug-cc-pV(Q+d)Z geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.027771	1.027771	1.027771
Cl	-1.027771	-1.027771	1.027771
Cl	-1.027771	1.027771	-1.027771
Cl	1.027771	-1.027771	-1.027771

CF₄

C	0.000000	0.000000	0.000000
F	0.765342	0.765342	0.765342
F	-0.765342	-0.765342	0.765342
F	-0.765342	0.765342	-0.765342
F	0.765342	-0.765342	-0.765342

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.174093	1.174093	1.174093
Cl	-1.174093	-1.174093	1.174093
Cl	-1.174093	1.174093	-1.174093
Cl	1.174093	-1.174093	-1.174093

SiF₄

Si	0.000000	0.000000	0.000000
F	0.903570	0.903570	0.903570
F	-0.903570	-0.903570	0.903570
F	-0.903570	0.903570	-0.903570
F	0.903570	-0.903570	-0.903570

B3LYP/def2-QZVPP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.027902	1.027902	1.027902
Cl	-1.027902	-1.027902	1.027902
Cl	-1.027902	1.027902	-1.027902
Cl	1.027902	-1.027902	-1.027902

CF₄

C	0.000000	0.000000	0.000000
F	0.765336	0.765336	0.765336
F	-0.765336	-0.765336	0.765336
F	-0.765336	0.765336	-0.765336
F	0.765336	-0.765336	-0.765336

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.174619	1.174619	1.174619
Cl	-1.174619	-1.174619	1.174619
Cl	-1.174619	1.174619	-1.174619
Cl	1.174619	-1.174619	-1.174619

SiF₄

Si	0.000000	0.000000	0.000000
F	0.903811	0.903811	0.903811
F	-0.903811	-0.903811	0.903811
F	-0.903811	0.903811	-0.903811
F	0.903811	-0.903811	-0.903811

B3LYP/MG3SXP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.028123	1.028123	1.028123
Cl	-1.028123	-1.028123	1.028123
Cl	-1.028123	1.028123	-1.028123
Cl	1.028123	-1.028123	-1.028123

CF₄

C	0.000000	0.000000	0.000000
F	0.764412	0.764412	0.764412
F	-0.764412	-0.764412	0.764412
F	-0.764412	0.764412	-0.764412
F	0.764412	-0.764412	-0.764412

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.174284	1.174284	1.174284
Cl	-1.174284	-1.174284	1.174284
Cl	-1.174284	1.174284	-1.174284
Cl	1.174284	-1.174284	-1.174284

SiF₄

Si	0.000000	0.000000	0.000000
F	0.902406	0.902406	0.902406
F	-0.902406	-0.902406	0.902406
F	-0.902406	0.902406	-0.902406
F	0.902406	-0.902406	-0.902406

M05-2X/aug-cc-pVQZ geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.019050	1.019050	1.019050
Cl	-1.019050	-1.019050	1.019050
Cl	-1.019050	1.019050	-1.019050
Cl	1.019050	-1.019050	-1.019050

CF₄

C	0.000000	0.000000	0.000000
F	0.761327	0.761327	0.761327
F	-0.761327	-0.761327	0.761327
F	-0.761327	0.761327	-0.761327
F	0.761327	-0.761327	-0.761327

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.170674	1.170674	1.170674
Cl	-1.170674	-1.170674	1.170674
Cl	-1.170674	1.170674	-1.170674
Cl	1.170674	-1.170674	-1.170674

SiF₄

Si	0.000000	0.000000	0.000000
F	0.901167	0.901167	0.901167
F	-0.901167	-0.901167	0.901167
F	-0.901167	0.901167	-0.901167
F	0.901167	-0.901167	-0.901167

M05-2X/6-311+G(3df,2p) geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.017546	1.017546	1.017546
Cl	-1.017546	-1.017546	1.017546
Cl	-1.017546	1.017546	-1.017546
Cl	1.017546	-1.017546	-1.017546

CF₄

C	0.000000	0.000000	0.000000
F	0.760347	0.760347	0.760347
F	-0.760347	-0.760347	0.760347
F	-0.760347	0.760347	-0.760347
F	0.760347	-0.760347	-0.760347

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.168312	1.168312	1.168312
Cl	-1.168312	-1.168312	1.168312
Cl	-1.168312	1.168312	-1.168312
Cl	1.168312	-1.168312	-1.168312

SiF₄

Si	0.000000	0.000000	0.000000
F	0.902226	0.902226	0.902226
F	-0.902226	-0.902226	0.902226
F	-0.902226	0.902226	-0.902226
F	0.902226	-0.902226	-0.902226

M05-2X/MG3S geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.018265	1.018265	1.018265
Cl	-1.018265	-1.018265	1.018265
Cl	-1.018265	1.018265	-1.018265
Cl	1.018265	-1.018265	-1.018265

CF₄

C	0.000000	0.000000	0.000000
F	0.761216	0.761216	0.761216
F	-0.761216	-0.761216	0.761216
F	-0.761216	0.761216	-0.761216
F	0.761216	-0.761216	-0.761216

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.169159	1.169159	1.169159
Cl	-1.169159	-1.169159	1.169159
Cl	-1.169159	1.169159	-1.169159
Cl	1.169159	-1.169159	-1.169159

SiF₄

Si	0.000000	0.000000	0.000000
F	0.898645	0.898645	0.898645
F	-0.898645	-0.898645	0.898645
F	-0.898645	0.898645	-0.898645
F	0.898645	-0.898645	-0.898645

M05-2X/def2-TZVPP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.017853	1.017853	1.017853
Cl	-1.017853	-1.017853	1.017853
Cl	-1.017853	1.017853	-1.017853
Cl	1.017853	-1.017853	-1.017853

CF₄

C	0.000000	0.000000	0.000000
F	0.761492	0.761492	0.761492
F	-0.761492	-0.761492	0.761492
F	-0.761492	0.761492	-0.761492
F	0.761492	-0.761492	-0.761492

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.169211	1.169211	1.169211
Cl	-1.169211	-1.169211	1.169211
Cl	-1.169211	1.169211	-1.169211
Cl	1.169211	-1.169211	-1.169211

SiF₄

Si	0.000000	0.000000	0.000000
F	0.900817	0.900817	0.900817
F	-0.900817	-0.900817	0.900817
F	-0.900817	0.900817	-0.900817
F	0.900817	-0.900817	-0.900817

M05-2X/aug-cc-pV(Q+d)Z geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.019050	1.019050	1.019050
Cl	-1.019050	-1.019050	1.019050
Cl	-1.019050	1.019050	-1.019050
Cl	1.019050	-1.019050	-1.019050

CF₄

C	0.000000	0.000000	0.000000
F	0.761327	0.761327	0.761327
F	-0.761327	-0.761327	0.761327
F	-0.761327	0.761327	-0.761327
F	0.761327	-0.761327	-0.761327

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.170674	1.170674	1.170674
Cl	-1.170674	-1.170674	1.170674
Cl	-1.170674	1.170674	-1.170674
Cl	1.170674	-1.170674	-1.170674

SiF₄

Si	0.000000	0.000000	0.000000
F	0.901167	0.901167	0.901167
F	-0.901167	-0.901167	0.901167
F	-0.901167	0.901167	-0.901167
F	0.901167	-0.901167	-0.901167

M05-2X/def2-QZVPP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.017995	1.017995	1.017995
Cl	-1.017995	-1.017995	1.017995
Cl	-1.017995	1.017995	-1.017995
Cl	1.017995	-1.017995	-1.017995

CF₄

C	0.000000	0.000000	0.000000
F	0.761396	0.761396	0.761396
F	-0.761396	-0.761396	0.761396
F	-0.761396	0.761396	-0.761396
F	0.761396	-0.761396	-0.761396

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.168952	1.168952	1.168952
Cl	-1.168952	-1.168952	1.168952
Cl	-1.168952	1.168952	-1.168952
Cl	1.168952	-1.168952	-1.168952

SiF₄

Si	0.000000	0.000000	0.000000
F	0.899982	0.899982	0.899982
F	-0.899982	-0.899982	0.899982
F	-0.899982	0.899982	-0.899982
F	0.899982	-0.899982	-0.899982

M05-2X/MG3SXP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.017952	1.017952	1.017952
Cl	-1.017952	-1.017952	1.017952
Cl	-1.017952	1.017952	-1.017952
Cl	1.017952	-1.017952	-1.017952

CF₄

C	0.000000	0.000000	0.000000
F	0.760345	0.760345	0.760345
F	-0.760345	-0.760345	0.760345
F	-0.760345	0.760345	-0.760345
F	0.760345	-0.760345	-0.760345

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.168283	1.168283	1.168283
Cl	-1.168283	-1.168283	1.168283
Cl	-1.168283	1.168283	-1.168283
Cl	1.168283	-1.168283	-1.168283

SiF₄

Si	0.000000	0.000000	0.000000
F	0.898799	0.898799	0.898799
F	-0.898799	-0.898799	0.898799
F	-0.898799	0.898799	-0.898799
F	0.898799	-0.898799	-0.898799

M06-2X/aug-cc-pVQZ geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.019840	1.019840	1.019840
Cl	-1.019840	-1.019840	1.019840
Cl	-1.019840	1.019840	-1.019840
Cl	1.019840	-1.019840	-1.019840

CF₄

C	0.000000	0.000000	0.000000
F	0.759852	0.759852	0.759852
F	-0.759852	-0.759852	0.759852
F	-0.759852	0.759852	-0.759852
F	0.759852	-0.759852	-0.759852

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.167716	1.167716	1.167716
Cl	-1.167716	-1.167716	1.167716
Cl	-1.167716	1.167716	-1.167716
Cl	1.167716	-1.167716	-1.167716

SiF₄

Si	0.000000	0.000000	0.000000
F	0.899612	0.899612	0.899612
F	-0.899612	-0.899612	0.899612
F	-0.899612	0.899612	-0.899612
F	0.899612	-0.899612	-0.899612

M06-2X/6-311+G(3df,2p) geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.018724	1.018724	1.018724
Cl	-1.018724	-1.018724	1.018724
Cl	-1.018724	1.018724	-1.018724
Cl	1.018724	-1.018724	-1.018724

CF₄

C	0.000000	0.000000	0.000000
F	0.758822	0.758822	0.758822
F	-0.758822	-0.758822	0.758822
F	-0.758822	0.758822	-0.758822
F	0.758822	-0.758822	-0.758822

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.165507	1.165507	1.165507
Cl	-1.165507	-1.165507	1.165507
Cl	-1.165507	1.165507	-1.165507
Cl	1.165507	-1.165507	-1.165507

SiF₄

Si	0.000000	0.000000	0.000000
F	0.900884	0.900884	0.900884
F	-0.900884	-0.900884	0.900884
F	-0.900884	0.900884	-0.900884
F	0.900884	-0.900884	-0.900884

M06-2X/MG3S geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.019539	1.019539	1.019539
Cl	-1.019539	-1.019539	1.019539
Cl	-1.019539	1.019539	-1.019539
Cl	1.019539	-1.019539	-1.019539

CF₄

C	0.000000	0.000000	0.000000
F	0.759579	0.759579	0.759579
F	-0.759579	-0.759579	0.759579
F	-0.759579	0.759579	-0.759579
F	0.759579	-0.759579	-0.759579

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.166370	1.166370	1.166370
Cl	-1.166370	-1.166370	1.166370
Cl	-1.166370	1.166370	-1.166370
Cl	1.166370	-1.166370	-1.166370

SiF₄

Si	0.000000	0.000000	0.000000
F	0.897212	0.897212	0.897212
F	-0.897212	-0.897212	0.897212
F	-0.897212	0.897212	-0.897212
F	0.897212	-0.897212	-0.897212

M06-2X/def2-TZVPP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.019250	1.019250	1.019250
Cl	-1.019250	-1.019250	1.019250
Cl	-1.019250	1.019250	-1.019250
Cl	1.019250	-1.019250	-1.019250

CF₄

C	0.000000	0.000000	0.000000
F	0.759997	0.759997	0.759997
F	-0.759997	-0.759997	0.759997
F	-0.759997	0.759997	-0.759997
F	0.759997	-0.759997	-0.759997

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.166422	1.166422	1.166422
Cl	-1.166422	-1.166422	1.166422
Cl	-1.166422	1.166422	-1.166422
Cl	1.166422	-1.166422	-1.166422

SiF₄

Si	0.000000	0.000000	0.000000
F	0.899489	0.899489	0.899489
F	-0.899489	-0.899489	0.899489
F	-0.899489	0.899489	-0.899489
F	0.899489	-0.899489	-0.899489

M06-2X/aug-cc-pV(Q+d)Z geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.018813	1.018813	1.018813
Cl	-1.018813	-1.018813	1.018813
Cl	-1.018813	1.018813	-1.018813
Cl	1.018813	-1.018813	-1.018813

CF₄

C	0.000000	0.000000	0.000000
F	0.759852	0.759852	0.759852
F	-0.759852	-0.759852	0.759852
F	-0.759852	0.759852	-0.759852
F	0.759852	-0.759852	-0.759852

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.165711	1.165711	1.165711
Cl	-1.165711	-1.165711	1.165711
Cl	-1.165711	1.165711	-1.165711
Cl	1.165711	-1.165711	-1.165711

SiF₄

Si	0.000000	0.000000	0.000000
F	0.898126	0.898126	0.898126
F	-0.898126	-0.898126	0.898126
F	-0.898126	0.898126	-0.898126
F	0.898126	-0.898126	-0.898126

M06-2X/def2-QZVPP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.018912	1.018912	1.018912
Cl	-1.018912	-1.018912	1.018912
Cl	-1.018912	1.018912	-1.018912
Cl	1.018912	-1.018912	-1.018912

CF₄

C	0.000000	0.000000	0.000000
F	0.759843	0.759843	0.759843
F	-0.759843	-0.759843	0.759843
F	-0.759843	0.759843	-0.759843
F	0.759843	-0.759843	-0.759843

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.166198	1.166198	1.166198
Cl	-1.166198	-1.166198	1.166198
Cl	-1.166198	1.166198	-1.166198
Cl	1.166198	-1.166198	-1.166198

SiF₄

Si	0.000000	0.000000	0.000000
F	0.898364	0.898364	0.898364
F	-0.898364	-0.898364	0.898364
F	-0.898364	0.898364	-0.898364
F	0.898364	-0.898364	-0.898364

M06-2X/MG3SXP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.019075	1.019075	1.019075
Cl	-1.019075	-1.019075	1.019075
Cl	-1.019075	1.019075	-1.019075
Cl	1.019075	-1.019075	-1.019075

CF₄

C	0.000000	0.000000	0.000000
F	0.758822	0.758822	0.758822
F	-0.758822	-0.758822	0.758822
F	-0.758822	0.758822	-0.758822
F	0.758822	-0.758822	-0.758822

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.165556	1.165556	1.165556
Cl	-1.165556	-1.165556	1.165556
Cl	-1.165556	1.165556	-1.165556
Cl	1.165556	-1.165556	-1.165556

SiF₄

Si	0.000000	0.000000	0.000000
F	0.897329	0.897329	0.897329
F	-0.897329	-0.897329	0.897329
F	-0.897329	0.897329	-0.897329
F	0.897329	-0.897329	-0.897329

M08-HX/aug-cc-pVQZ geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.020061	1.020061	1.020061
Cl	-1.020061	-1.020061	1.020061
Cl	-1.020061	1.020061	-1.020061
Cl	1.020061	-1.020061	-1.020061

CF₄

C	0.000000	0.000000	0.000000
F	0.761818	0.761818	0.761818
F	-0.761818	-0.761818	0.761818
F	-0.761818	0.761818	-0.761818
F	0.761818	-0.761818	-0.761818

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.168043	1.168043	1.168043
Cl	-1.168043	-1.168043	1.168043
Cl	-1.168043	1.168043	-1.168043
Cl	1.168043	-1.168043	-1.168043

SiF₄

Si	0.000000	0.000000	0.000000
F	0.904056	0.904056	0.904056
F	-0.904056	-0.904056	0.904056
F	-0.904056	0.904056	-0.904056
F	0.904056	-0.904056	-0.904056

M08-HX/6-311+G(3df,2p) geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.020960	1.020960	1.020960
Cl	-1.020960	-1.020960	1.020960
Cl	-1.020960	1.020960	-1.020960
Cl	1.020960	-1.020960	-1.020960

CF₄

C	0.000000	0.000000	0.000000
F	0.761101	0.761101	0.761101
F	-0.761101	-0.761101	0.761101
F	-0.761101	0.761101	-0.761101
F	0.761101	-0.761101	-0.761101

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.169701	1.169701	1.169701
Cl	-1.169701	-1.169701	1.169701
Cl	-1.169701	1.169701	-1.169701
Cl	1.169701	-1.169701	-1.169701

SiF₄

Si	0.000000	0.000000	0.000000
F	0.903707	0.903707	0.903707
F	-0.903707	-0.903707	0.903707
F	-0.903707	0.903707	-0.903707
F	0.903707	-0.903707	-0.903707

M08-HX/MG3S geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.019731	1.019731	1.019731
Cl	-1.019731	-1.019731	1.019731
Cl	-1.019731	1.019731	-1.019731
Cl	1.019731	-1.019731	-1.019731

CF₄

C	0.000000	0.000000	0.000000
F	0.761957	0.761957	0.761957
F	-0.761957	-0.761957	0.761957
F	-0.761957	0.761957	-0.761957
F	0.761957	-0.761957	-0.761957

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.166664	1.166664	1.166664
Cl	-1.166664	-1.166664	1.166664
Cl	-1.166664	1.166664	-1.166664
Cl	1.166664	-1.166664	-1.166664

SiF₄

Si	0.000000	0.000000	0.000000
F	0.902051	0.902051	0.902051
F	-0.902051	-0.902051	0.902051
F	-0.902051	0.902051	-0.902051
F	0.902051	-0.902051	-0.902051

M08-HX/def2-TZVPP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.019272	1.019272	1.019272
Cl	-1.019272	-1.019272	1.019272
Cl	-1.019272	1.019272	-1.019272
Cl	1.019272	-1.019272	-1.019272

CF₄

C	0.000000	0.000000	0.000000
F	0.762202	0.762202	0.762202
F	-0.762202	-0.762202	0.762202
F	-0.762202	0.762202	-0.762202
F	0.762202	-0.762202	-0.762202

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.166412	1.166412	1.166412
Cl	-1.166412	-1.166412	1.166412
Cl	-1.166412	1.166412	-1.166412
Cl	1.166412	-1.166412	-1.166412

SiF₄

Si	0.000000	0.000000	0.000000
F	0.903573	0.903573	0.903573
F	-0.903573	-0.903573	0.903573
F	-0.903573	0.903573	-0.903573
F	0.903573	-0.903573	-0.903573

M08-HX/aug-cc-pV(Q+d)Z geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.021194	1.021194	1.021194
Cl	-1.021194	-1.021194	1.021194
Cl	-1.021194	1.021194	-1.021194
Cl	1.021194	-1.021194	-1.021194

CF₄

C	0.000000	0.000000	0.000000
F	0.761466	0.761466	0.761466
F	-0.761466	-0.761466	0.761466
F	-0.761466	0.761466	-0.761466
F	0.761466	-0.761466	-0.761466

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.169675	1.169675	1.169675
Cl	-1.169675	-1.169675	1.169675
Cl	-1.169675	1.169675	-1.169675
Cl	1.169675	-1.169675	-1.169675

SiF₄

Si	0.000000	0.000000	0.000000
F	0.900888	0.900888	0.900888
F	-0.900888	-0.900888	0.900888
F	-0.900888	0.900888	-0.900888
F	0.900888	-0.900888	-0.900888

M08-HX/def2-QZVPP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.022264	1.022264	1.022264
Cl	-1.022264	-1.022264	1.022264
Cl	-1.022264	1.022264	-1.022264
Cl	1.022264	-1.022264	-1.022264

CF₄

C	0.000000	0.000000	0.000000
F	0.761466	0.761466	0.761466
F	-0.761466	-0.761466	0.761466
F	-0.761466	0.761466	-0.761466
F	0.761466	-0.761466	-0.761466

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.171685	1.171685	1.171685
Cl	-1.171685	-1.171685	1.171685
Cl	-1.171685	1.171685	-1.171685
Cl	1.171685	-1.171685	-1.171685

SiF₄

Si	0.000000	0.000000	0.000000
F	0.902674	0.902674	0.902674
F	-0.902674	-0.902674	0.902674
F	-0.902674	0.902674	-0.902674
F	0.902674	-0.902674	-0.902674

M08-HX/MG3SXP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.021685	1.021685	1.021685
Cl	-1.021685	-1.021685	1.021685
Cl	-1.021685	1.021685	-1.021685
Cl	1.021685	-1.021685	-1.021685

CF₄

C	0.000000	0.000000	0.000000
F	0.761101	0.761101	0.761101
F	-0.761101	-0.761101	0.761101
F	-0.761101	0.761101	-0.761101
F	0.761101	-0.761101	-0.761101

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.169839	1.169839	1.169839
Cl	-1.169839	-1.169839	1.169839
Cl	-1.169839	1.169839	-1.169839
Cl	1.169839	-1.169839	-1.169839

SiF₄

Si	0.000000	0.000000	0.000000
F	0.900277	0.900277	0.900277
F	-0.900277	-0.900277	0.900277
F	-0.900277	0.900277	-0.900277
F	0.900277	-0.900277	-0.900277

M08-SO/aug-cc-pVQZ geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.022264	1.022264	1.022264
Cl	-1.022264	-1.022264	1.022264
Cl	-1.022264	1.022264	-1.022264
Cl	1.022264	-1.022264	-1.022264

CF₄

C	0.000000	0.000000	0.000000
F	0.761466	0.761466	0.761466
F	-0.761466	-0.761466	0.761466
F	-0.761466	0.761466	-0.761466
F	0.761466	-0.761466	-0.761466

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.171685	1.171685	1.171685
Cl	-1.171685	-1.171685	1.171685
Cl	-1.171685	1.171685	-1.171685
Cl	1.171685	-1.171685	-1.171685

SiF₄

Si	0.000000	0.000000	0.000000
F	0.902674	0.902674	0.902674
F	-0.902674	-0.902674	0.902674
F	-0.902674	0.902674	-0.902674
F	0.902674	-0.902674	-0.902674

M08-SO/6-311+G(3df,2p) geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.020960	1.020960	1.020960
Cl	-1.020960	-1.020960	1.020960
Cl	-1.020960	1.020960	-1.020960
Cl	1.020960	-1.020960	-1.020960

CF₄

C	0.000000	0.000000	0.000000
F	0.761101	0.761101	0.761101
F	-0.761101	-0.761101	0.761101
F	-0.761101	0.761101	-0.761101
F	0.761101	-0.761101	-0.761101

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.169701	1.169701	1.169701
Cl	-1.169701	-1.169701	1.169701
Cl	-1.169701	1.169701	-1.169701
Cl	1.169701	-1.169701	-1.169701

SiF₄

Si	0.000000	0.000000	0.000000
F	0.903707	0.903707	0.903707
F	-0.903707	-0.903707	0.903707
F	-0.903707	0.903707	-0.903707
F	0.903707	-0.903707	-0.903707

M08-SO/MG3S geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.022038	1.022038	1.022038
Cl	-1.022038	-1.022038	1.022038
Cl	-1.022038	1.022038	-1.022038
Cl	1.022038	-1.022038	-1.022038

CF₄

C	0.000000	0.000000	0.000000
F	0.761744	0.761744	0.761744
F	-0.761744	-0.761744	0.761744
F	-0.761744	0.761744	-0.761744
F	0.761744	-0.761744	-0.761744

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.170745	1.170745	1.170745
Cl	-1.170745	-1.170745	1.170745
Cl	-1.170745	1.170745	-1.170745
Cl	1.170745	-1.170745	-1.170745

SiF₄

Si	0.000000	0.000000	0.000000
F	0.900545	0.900545	0.900545
F	-0.900545	-0.900545	0.900545
F	-0.900545	0.900545	-0.900545
F	0.900545	-0.900545	-0.900545

M08-SO/def2-TZVPP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.017852	1.017852	1.017852
Cl	-1.017852	-1.017852	1.017852
Cl	-1.017852	1.017852	-1.017852
Cl	1.017852	-1.017852	-1.017852

CF₄

C	0.000000	0.000000	0.000000
F	0.761492	0.761492	0.761492
F	-0.761492	-0.761492	0.761492
F	-0.761492	0.761492	-0.761492
F	0.761492	-0.761492	-0.761492

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.165728	1.165728	1.165728
Cl	-1.165728	-1.165728	1.165728
Cl	-1.165728	1.165728	-1.165728
Cl	1.165728	-1.165728	-1.165728

SiF₄

Si	0.000000	0.000000	0.000000
F	0.897318	0.897318	0.897318
F	-0.897318	-0.897318	0.897318
F	-0.897318	0.897318	-0.897318
F	0.897318	-0.897318	-0.897318

M08-SO/aug-cc-pV(Q+d)Z geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.021194	1.021194	1.021194
Cl	-1.021194	-1.021194	1.021194
Cl	-1.021194	1.021194	-1.021194
Cl	1.021194	-1.021194	-1.021194

CF₄

C	0.000000	0.000000	0.000000
F	0.761466	0.761466	0.761466
F	-0.761466	-0.761466	0.761466
F	-0.761466	0.761466	-0.761466
F	0.761466	-0.761466	-0.761466

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.169675	1.169675	1.169675
Cl	-1.169675	-1.169675	1.169675
Cl	-1.169675	1.169675	-1.169675
Cl	1.169675	-1.169675	-1.169675

SiF₄

Si	0.000000	0.000000	0.000000
F	0.900888	0.900888	0.900888
F	-0.900888	-0.900888	0.900888
F	-0.900888	0.900888	-0.900888
F	0.900888	-0.900888	-0.900888

M08-SO/def2-QZVPP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.018908	1.018908	1.018908
Cl	-1.018908	-1.018908	1.018908
Cl	-1.018908	1.018908	-1.018908
Cl	1.018908	-1.018908	-1.018908

CF₄

C	0.000000	0.000000	0.000000
F	0.758811	0.758811	0.758811
F	-0.758811	-0.758811	0.758811
F	-0.758811	0.758811	-0.758811
F	0.758811	-0.758811	-0.758811

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.165728	1.165728	1.165728
Cl	-1.165728	-1.165728	1.165728
Cl	-1.165728	1.165728	-1.165728
Cl	1.165728	-1.165728	-1.165728

SiF₄

Si	0.000000	0.000000	0.000000
F	0.897318	0.897318	0.897318
F	-0.897318	-0.897318	0.897318
F	-0.897318	0.897318	-0.897318
F	0.897318	-0.897318	-0.897318

M08-SO/MG3SXP geometries

CCl₄

C	0.000000	0.000000	0.000000
Cl	1.021685	1.021685	1.021685
Cl	-1.021685	-1.021685	1.021685
Cl	-1.021685	1.021685	-1.021685
Cl	1.021685	-1.021685	-1.021685

CF₄

C	0.000000	0.000000	0.000000
F	0.761101	0.761101	0.761101
F	-0.761101	-0.761101	0.761101
F	-0.761101	0.761101	-0.761101
F	0.761101	-0.761101	-0.761101

SiCl₄

Si	0.000000	0.000000	0.000000
Cl	1.169839	1.169839	1.169839
Cl	-1.169839	-1.169839	1.169839
Cl	-1.169839	1.169839	-1.169839
Cl	1.169839	-1.169839	-1.169839

SiF₄

Si	0.000000	0.000000	0.000000
F	0.900277	0.900277	0.900277
F	-0.900277	-0.900277	0.900277
F	-0.900277	0.900277	-0.900277
F	0.900277	-0.900277	-0.900277

Table ESI-2. Energies (kcal/mol). This table contains the Born-Oppenheimer energies of reaction corresponding to the enthalpies of reaction at 298 K that underlie Table 2. The Born-Oppenheimer energies consist of the electronic energy plus nuclear repulsion, and they are independent of temperature.

Basis	B3LYP	M05-2X	M06-2X	M08-HX	M08-SO	XYG3
aug-cc-pVQZ	-19.6	-30.7	-21.8	-30.0	-23.1	-23.2
6-311+G(3df,2p)	-15.7	-23.5	-14.2	-23.8	-21.2	-17.2
MG3S	-20.5	-28.3	-18.6	-25.4	-27.3	-23.0
def2-TZVPP	-18.7	-28.7	-19.7	-31.3	-22.3	-20.1
aug-cc-pV(Q+d)Z	-22.1	-32.9	-23.9	-32.0	-25.4	-25.1
def2-QZVPP	-21.7	-32.2	-23.0	-31.3	-24.9	-22.7
MG3SXP	-20.7	-28.2	-19.1	-28.0	-25.5	-22.1

Table ESI-3. Enthalpies of reaction at 0 K (kcal/mol)

Basis	B3LYP	M05-2X	M06-2X	M08-HX	M08-SO	XYG3
aug-cc-pVQZ	-21.0	-23.2	-21.2	-31.5	-24.6	-24.7
6-311+G(3df,2p)	-17.1	-24.9	-15.7	-25.4	-22.7	-18.7
MG3S	-21.9	-29.6	-20.0	-26.9	-28.8	-24.5
def2-TZVPP	-20.1	-30.0	-21.2	-32.9	-23.9	-21.6
aug-cc-pV(Q+d)Z	-23.5	-34.2	-25.3	-33.6	-26.9	-26.6
def2-QZVPP	-23.1	-33.4	-23.2	-32.9	-26.5	-24.2
MG3SXP	-22.1	-29.5	-25.3	-26.5	-27.0	-23.6